PYROLYSIS AND PROPENSITY TO SELF IGNITION OF LONG-TERM LOW-TEMPERATURE WOOD CHARS

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TABLE OF CONTENTS

SUMMARY

Cases have shown that when wood was exposed to long-term low temperature heat sources with different oxygen exposure conditions; it turned into reactive chars that carried fire risk. However, there is still little experimental data explaining the pyrolysis process and reactivity of these chars. This thesis provided a comprehensive study with experimental evidences on the pyrolysis and propensity to self ignition of long-term low-temperature wood chars.

Pyrolysis experiments were carried out on Kapur and Nyatoh hardwood species in ovens isothermally at low temperatures 160 °C, 175 °C and 190 °C for extended durations up to 153 days in both anaerobic and aerobic conditions. Empirical pyrolysis kinetic models of Nyatoh and Kapor wood under isothermal conditions in air were developed based on weight loss history of the pyrolysis process. Thermo-gravimetric analysis (TGA) and Fourier Transform Infrared spectroscopy (FTIR) were employed as analytical methods to determine the oxygen chemisorption and functionality of these chars.

It was shown that except for the initial fast degradation, the wood degraded following a first order reaction process. The activation energies of the two kinds of hardwood used in this study were different although these values were still in the range reported in literature. The difference could be explained by the different chemical composition with different proportion of cellulose, hemicelluloses and lignin presenting in each wood specie.

Chars created at low temperature for long duration in both aerobic and anaerobic conditions were proved to be reactive and susceptible to oxygen chemisorptions. These chars carried the potential of self ignition. Under the same exposure

conditions, anaerobic wood char had higher initial rate of oxygen chemisorptions, in other words, it is evidenced that anaerobic chars are more reactive. Through FTIR investigation, anaerobic chars had more reactive aliphatic groups, especially aliphatic α-CH_2. For less reactive aerobic char, it was believed that benzylic and hydroaromatic groups were the reactive sites responsible for the oxygen chemisorption.

The reactivity of the chars increased with the degree of pyrolysis, the char reactivity would reach the highest at charcoal condition with the final weight around 19-25%. The pyrolysis kinetic model could be used to obtain the rough estimate of the heating period to reach different degrees of degradation under air condition as a function of temperature of Nyatoh and Kapor wood.

The theoretical understanding had practical meaning to the extensive use of wood in related to fire safety and fire protection.

The results of the thesis have been published in the following conferences and journal:

1. N. Q. A. Hoang and M. Y. L. Chew, "Experimental findings on char characterization of pyrophoric chars," in *7th Asia-Oceania Symposium on Fire Science and Technology* Hong Kong, 2007. (Poster presentation)

2. N. Q. A. Hoang and M. Y. L. Chew, "Propensity of low-temperature and anaerobic and aerobic wood chars to self ignition " in *Fire and Material Conference 2009* San Francisco, 2009. (Conference article)

3. N. Q. A. Hoang and M. Y. L. Chew, "Pyrolysis of tropical hardwood under long-term and low-temperature conditions," *Construction and Building Materials,* 2009. (in proceeding)

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

Introduction

1.1. Background

As trees covers most habitable area of the Earth, wood has become the most familiar material to human being. In the past, wood was used extensively in house building, working tools and ship making due to its durability and availability. Nowadays, wood still plays an important role in everyday life. Hundreds of things made from wood can be found anywhere like stationary (pencils, paper…), accessories and furniture. Wood are still used as building components like beams, posts, doors, windows, flooring, ceiling or wall lining. Wood is very useful to human life; however, it is also known as a flammable material and carries fire risk. Every year, in some countries like Australia and Indonesia, bushfires break out and cause a lot of damage in hot and dry season. Wood materials easily catch fire and make the fire more severe.

Usually, wood ignites when it is provided enough heat and oxygen. The short-term ignition of wood requires the temperature to be raised to approximately 250°C [1]. In many other cases, the auto-ignition or spontaneous ignition temperature of wood is reported as high as 600°C by radiation and 490°C by conduction respectively [2]. Thus, in normal practice, little precautions have been taken when wood is in proximity to much lower temperatures. However, some fire incidents still happened due to the self ignition of wood at below 200°C and the

lowest ignition temperature was reported at 77°C [3]. These were the cases when wood were in contact with low level heat sources like hot water pipes, hot operating machines and hot air ducts. Ignition occurred after wood self heated at low temperatures for a long period of time and built heat inside the material through exothermic reactions. The duration may vary from 3 months to 15 years [3] depending on many factors including exposure temperature and oxygen condition. In average, air is comprised of 21 percent oxygen, however, in lower-concentrated oxygen environment, self-heating can still happen when the surrounding environment is at a relatively low temperature [4].

1.2. Research problems and objectives

The propensity of self ignition of wood material after being self heated for a period of time has interested many researchers. McNaughton [5] carried out experimental tests on the weight loss of small wood samples at low temperatures for extended durations, however, the tests were restricted to only observations and descriptions. Stamm [6] did more in-depth analysis on rate of thermal degradation, yet, he only used the data of cellulose, cotton and some softwood species. Recently, the studies of thermal degradation have been mainly conducted on chars created at pretty high temperatures (above 300°C) for very short durations. There is still a lack of research results for wood chars created at long-term low-temperature conditions which are closed to self-heating situations in order to prevent and control unwanted fire cases. This thesis provides the experimental study on long-term low-temperature wood chars with the following goals:

1. **To develop empirical pyrolysis kinetic model of hardwood chars heated in air at low temperatures (below 200°C) based on weight loss during the degradation process**. Data were collected on different species of hardwood. The study seeks to establish the rates of pyrolysis of different species of hardwood at low temperatures and the reaction order that corresponds to these rates and thus estimate the heating duration to reach different degrees of degradation as a function of temperature.

2. **To compare the chemisorption characteristics and reactivity of aerobic and anaerobic wood chars and investigate their propensity to self ignition**. The reactivity of chars can be measured by the rate of chemisorption [6]. There are many studies about the reactivity of carbon and cellulosic chars created at different temperatures and oxygen conditions, however, little is known about the reactivity of wood chars created under low temperature in both anaerobic and aerobic conditions. It is not accurate to extrapolate the chemisorption data of carbon or cellulosic chars to wood chars, this is because wood also contains hemicelluloses, lignin and a small amount of inorganic constituents, other than cellulose. Thermo-gravimetric analysis (TGA) was employed to determine the chemisorption characteristics of the chars. Rates of oxygen uptake and activation energies were calculated using Elovich kinetics and Arrhenius equation to describe the types of reactive sites presenting in the wood char.

3. **To examine the chemical effects involved in pyrolysis and oxygen chemisorption of wood chars**. Fourier-transform infrared (FTIR) spectroscopy was used as an analytical method to detect the changes in functional groups. It has been pointed out that functional groups other than free radicals could play a major

role in determining the functionality and reactivity of the char [7]. In this study, the development of functional groups in wood during pyrolysis process was investigated. The functionality changes of wood chars when exposed to air during oxygen chemisorption experiments provide the explanations for the bulk-scale chemisorption behaviour and help to identify the reactive groups.

1.3. Organisation of the study

The study was organized as follows:

Chapter 1 described the background concerning the potential hazards to fire in general and to self ignition in particular of wood materials. The background provided the basis understanding on the usage of wood and the cases leading to self ignition. The research problems and research objectives were indentified in connection with the gaps identified in Chapter 2 of Literature Review.

Chapter 2 reviewed the literature. The chapter differentiated self ignition to gas-phase ignition and evaluated the possibility of self heating and self ignition of wood materials in different oxygen conditions. The pyrolysis process of wood and its kinetics were discussed. The details of functionality and its effects on chemisorption were described. The chapter also highlighted the role of chemisorption and discussed the application of Elovich kinetic model to oxygen chemisorption of lignocellulosic materials.

Chapter 3 discussed the research methodology on wood pyrolysis and char characterization. The chapter first described pyrolysis experiments with the careful

selection of materials. It then presented the two analytical methods to characterize the pyrolyzed wood chars. This included the measurements of functional groups using FTIR and the measurements of oxygen chemisorption using TGA. Discussions of the principles of each technique and subsequent experimental procedures were provided.

Chapter 4 presented the results of wood pyrolysis. The visible physical changes including wood colour, shrinkage and cracks after heated in ovens at low temperatures for extended durations were described in details. Besides, an attempt was made to determine the kinetics of thermal degradation Nyatoh and Kapor wood in air using the weight loss data throughout the degradation process.

Chapter 5 analyzed the characterization of wood chars based on FTIR and TGA results. Functional group changes during heat treatments and oxygen chemisorption were presented. The effects of oxygen chemisorption to the char functionality were investigated to provide an insight to the changes in the chemical bonds attributed to the oxygen chemisorption process. Besides, the differences in reactivity between aerobic and anaerobic wood chars were examined.

Finally, Chapter 6 presented the research findings and recommendations for future works.

CHAPTER 2

LITERATURE REVIEW

2.1. Introduction

A great deal of previous studies existed in the research literature showed the self ignition properties of lignocellulosic materials. The review of this study focused primarily on the reports and research done on the pyrolysis and self-ignition of solid wood members. Firstly, the chapter justified the fire hazards of wood material due to self ignition. The remaining part of the chapter was sectioned according to the three main scopes and objectives of the study including: pyrolysis of wood at low temperatures, functionality of the wood chars and chemisorption characteristics of these chars. The review provided in this chapter proved the need for this study.

2.2. Self ignition

2.2.1. Self ignition and gas-phase ignition

Self ignition and piloted or auto-ignition of wood have totally different mechanism. To research on the propensity of self ignition, it is essential to distinguish between self ignition and piloted or auto-ignition because the causes leading to piloted and auto-ignition may not applicable to self ignition.

According to NFPA 921 Guide for Fire and Explosion Investigations [4], self ignition arises from self heating which is the result of internal reactions and processes producing sufficient heat under satisfactory conditions . In the concern of this study, the reactions and processes involved are the exothermic chemical

reactions including exothermic pyrolysis or surface oxidation reactions [8], as a consequence self ignition can be called solid-phase ignition. Self ignition occurs at relatively low temperatures (100 to 200 °C or even below) after a long period of heat generation [9]. Self ignition is also called spontaneous ignition or spontaneous combustion.

In case of normal ignition, a spark or flame helps to initiate the piloted ignition process while auto-ignition occurs without any spark or flame source. Both piloted ignition and auto –ignition have the same fashion of ignition: when subjected to the high heat source, wood will give off combustible gases; these gaseous products are then mixed with air and react with oxygen leading to ignition in the gas phase, so they are also called gas-phase ignition [8].

2.2. 2. Self-heating of wood materials

Schwartz [10] stated in his book in 1901 that "...wood exhibits a certain weakness that is not shared by iron or metal, namely, the tendency to ignite spontaneously when exposed to the protracted influence of a source of small external heat". In 1911, the Independent Inspection Bureau [11] reported more than a dozen of fires started by low pressure steam pipes in a NFPA Quarterly volume 4. As in the concern of this study, self-heating required the heat from exothermic pyrolysis or surface oxidation reactions, the access of oxygen into the material helped to sustain the oxidation reactions and pyrolysis process. Thus, porous forms of materials obviously supported self-heating more than those in solid forms. The porous forms of wood material included wood sawdust, wood fibreboard and wood chips and solid forms included wood beams and wood posts. In historical record of self ignition, many cases were reported on the self-heating of piles of porous haystacks

[12] or charcoal. A fire breakout due to self-ignition of wood fibreboard during storage and transport in 1950 was recorded by Mitchelle [13]. Before ignition, the fibreboard was found to stack in one pile in the warehouse measuring more than 24,000 cubic feet when the surrounding air was at about 75 °F (24 °C).

Still, cases of self ignition of solid wood members have been reported in many studies. Most of the cases originated from prolonged contact of wood members with heat sources like hot steam pipes, hot water pipes and other hot surfaces in the temperature range 100-170°C [8]. Schwartz [10] listed the possible circumstances leading to self heating and outbreaks of fire which included: "a lamp hanging too near a beam; a steam pipe or hot air pipe laid too close to woodwork; dust settling down in thick layers on heated vessels or pipes; defective insulating material around a steam pipe, stove, fireplace, drying plant, and more, which are thereby enabled to radiate heat continuously against wooden articles". He also found that high temperatures were unnecessary but the prolonged exposure played as a crucial factor. Bixel and Moore [14] reported self ignition of a wood beam due to hot steam pipe drilled through it, the exposure time was from 3 months to 3 years prior to ignition. The duration might be up to 15 years as reported by Matson et al. [15]. Nailen [16] also reported a fire case when wood joists were placed near a hot-water radiator.

McGuire [17] suggested that generation of charcoal constituted a hazard associated with subsequent self heating in the cases of fires arising from steam pipes. This was in good agreement with Schaffer's study [18], at a temperature range between 100 °C and about 280 °C, the wood underwent slow pyrolysis process characterizing by losing weight slowly and turning into charcoal eventually. He

also stated that the formation of charcoal in the thermal degradation was a significant factor in self-heating process and initiation of flaming combustion. Shafizadeh and Bradbury [19] found that cellulosic chars produced during low-temperature pyrolysis were highly reactive as compared to graphite and other forms of pure carbon.

Recently, studies of Cuzzillo and Pagni [20, 21] proved that solid wood members exposed to heat would be more permeable and allowed the diffusion of oxygen. Cuzzillo conducted experiments on whole wood self-heating. When heated isothermally in oven at 200 °C, an 89 mm (3.5") wood cube reached thermal runaway after around 250 minutes. Figure 2.1 revealed transverse shrinkage and cracks on end-grain surfaces and Figure 2.2 showed an hourglass pattern with the bell mouths at the end-grain surfaces of the cube when it was split along the longitudinal grain. These results indicated that more heat was generated at end-grain surface than at side-grain surface of the wood cube. When sealing the end-grain surfaces of the 200 mm wood cube as shown in Figure 2.3 and heated it in the oven at 200 °C, this cube exhibited thermal runaway after 9 days while the same unsealed cube ignited after 1 days, this indicated that oxygen could also diffuse through the side-grain surfaces. It was obvious that solid wood members which were exposed to heat for a long period of time reduced conductivity and increased porosity. Besides, the cracks on the surfaces allowed more oxygen to access into the char created inside [22].

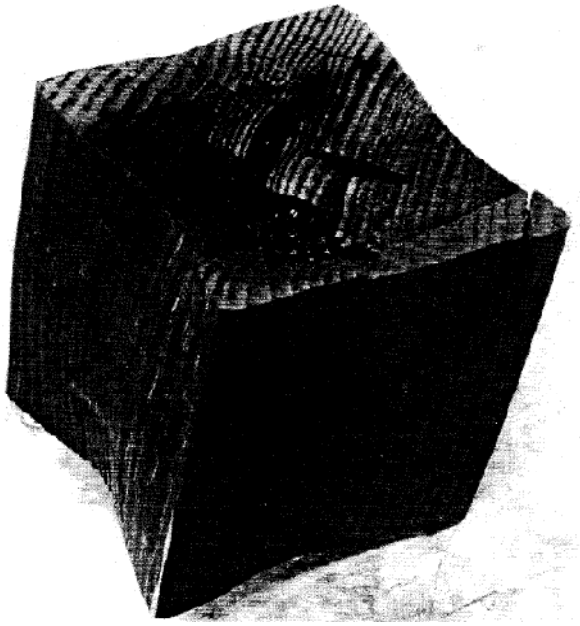


Figure 2.1. An 89 mm wood cube after self-heating at 200 °C (Reprinted from B. R. Cuzzillo, "Pyrophoria," in *Mechanical Engineering*, Doctor of Philosophy Berkeley: University of California, 1997, p. 182*)*

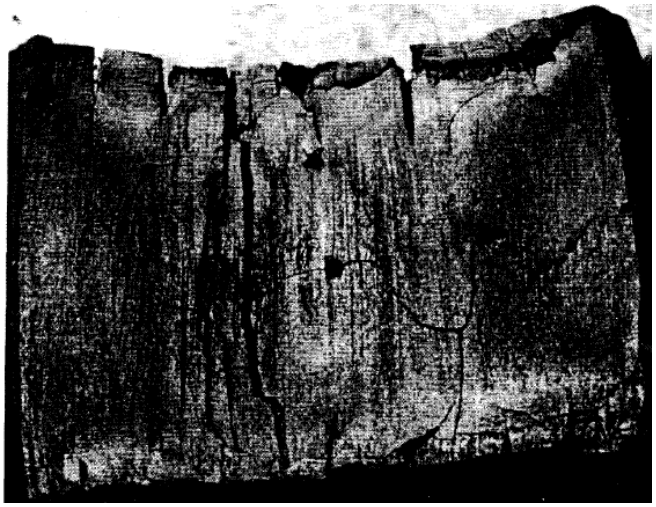


Figure 2.2. Hourglass heat pattern of an 89 mm wood cube split along longitudinal grain after self-heating (Reprinted from B. R. Cuzzillo, "Pyrophoria," in *Mechanical Engineering*, Doctor of Philosophy Berkeley: University of California, 1997, p. 182*)*

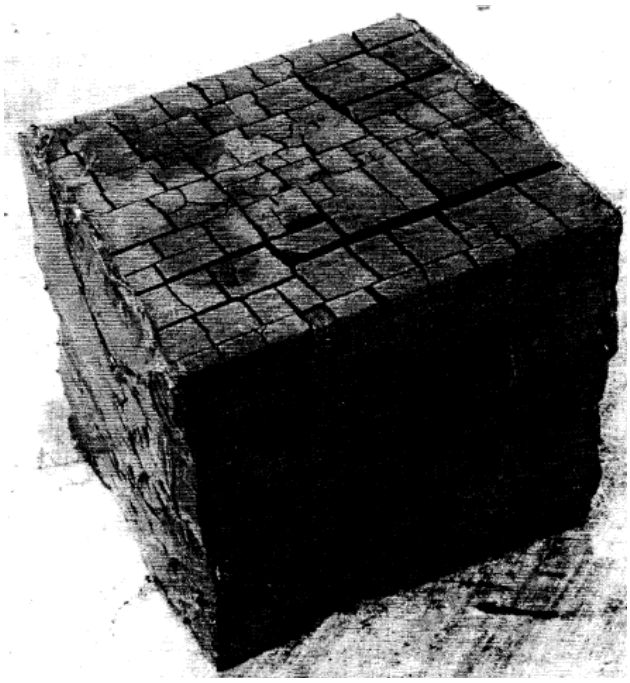


Figure 2.3. 200mm wood cube after9 days at 200 °C with the end-grain faces sealed with RTV (Reprinted from B. R. Cuzzillo, "Pyrophoria," in *Mechanical Engineering*, Doctor of Philosophy Berkeley: University of California, 1997, p. 182*)*

2.2.3. Self ignition in limited oxygen conditions

Among the external variables, apart from temperature and duration of heat generation, oxygen condition is also an important factor that affects the propensity to self ignition of wood materials. The oxygen condition can affect both the reaction rate and kinetic order of reaction during degradation process [23]. Bowes [24] observed that wood char created in the lack of air could have properties of chemically activated carbon like charcoal and might self ignite when exposed to air. He suggested that char created in the absence of air was more reactive in the following paragraph:

> "Certainly, wood exposed to temperatures not far excess of 100 °C can be converted to charcoal after very long periods, but in most cases this takes

> place in the continuous presence of air and it does not follow that the resulting charcoal will have the self-ignition properties of fresh charcoal produced in the absence of air." [p. 353]
>
> "… If charring could take place in the absence of air, ignition might occur at quite low temperatures if air were to be subsequently admitted. As an extreme example, it may be calculated that, if a 50 mm x 100 mm beam could be converted to charcoal with the properties of chemically activated carbon, in the absence of air, self-ignition on exposure to air could occur at a uniform ambient temperature of 111 °C." [p. 357]

Fred Shafizadeh [25, 26] also showed that oxidation reactions of the anaerobic chars produced higher exothermicity than aerobic char did. John DeHaan [22] and Babraukas [8] reported cases of fires where wood members were covered by a sheet of metal or a tile. This layer would prevent the penetration of air into the wood member below but it still allowed heat to pass through, thus, maintained the decomposition process. Highly reactive chars like charcoal would be created and with the sudden admission of oxygen through cracks or collapse due to wood shrinkage, ignition might happen. Martin and Margot [27] revealed that the whole process could take 5 to 10 years prior to ignition and the wood member had to be rather massive.

Similarly, Kubler [28] described the process of self-heating of wood-base panels packing tight together with little access of oxygen during transportation and storage as followed: When the wood panels were stacked too hot together in packs, heat of pyrolysis accumulated and raised the temperature deep inside the packs, the wood here gradually turned into darkening brittle materials, and finally into black

charcoal. Cracks were formed due to contraction of charring and volatilization. Cavities developed inside the packs, grew in all directions and approached the surface of wood panels. Air could then diffuse into the hot char formed inside the packs through cracks and cavities and started ignition.

2.3. Pyrolysis of wood at low temperatures

The word “pyrolysis” origins from two Greek words: “pyro” (fire) and “lysys” (decomposition). Pyrolysis is the process of thermal decomposition under the effect of heat. The pyrolysis of wood has received great concern as this combustible material is the cause of a lot of fires.

Wood is a complex compound with the chemical composition includes cellulose (40-50%), hemicelluloses (15-25%) and lignin (15-35%) and a small amount of inorganic salts. This chemical composition varies depending on different species of wood. Due to different constituents, the pyrolysis of wood is also a complex process with different reactions such as cracking, depolymerisation and devolatilization. Each constituent pyrolyzes at different temperature, hemicelluloses decomposes first at 200 °C to 260 °C following by cellulose at 240 °C to 300 °C and finally lignin at 280 °C to 500 °C [29]. At high temperature above 200 °C, wood pyrolyzes fast into char (solid residue), tar and low-molecular gases like CH_4, CO, CO_2, H_2 and H_2O. The gases evaporate and mix with air in the surrounding, if the heat provided is high enough, the mixture erupted into flaming combustion. The charcoal can burn through exothermic reactions with oxygen and lead to glowing combustion. At below 200 °C, heating wood material for long duration will produce the same effects, thus, the ignition temperature of wood is not fixed and may vary depending on the intensity and the rate of heat application [22].

Schwartz [10] described the long-term low-temperature pyrolysis of wood as follows :

> "On prolonging the exposure to heat, without increasing the temperature beyond the point just necessary to drive out all the moisture (80 °C-110 °C usually suffices), the dried material, the main substance of which remains unchanged, sustains under the protracted influence of the heat a certain amount of alteration in its subordinate constituents, *e.g.* in the case of wood, the resinous matters, dried sap constituents… Later on, the alteration becomes apparent externally, commencing with a slight browning, which gradually develops into charring, accompanied by the formation of gaseous products like carbon dioxide, carbon monoxide and hydrocarbons of various kinds, the material itself becoming higher in carbon". [pp. 162-163]

The experiments conducted by McNaughton [5] in 1944 on the pyrolysis of small maple wood blocks isothermally at various low temperatures in the range from 107 °C to 150 °C for various extended periods in electrically controlled drying ovens followed the same procedure, the results were summarized in Table 2.1. Ignition did not happen to all the samples. The thermal degradation of the samples was observed to be not associated with any one critical temperature but all samples lost weight at a regular rate at each temperature, the weight lost faster at higher temperature. For example, wood samples lost 15% of weight after heated at 107 °C for 1050 days and turned into chocolate colour, the same effect happened to wood samples heated at 120 °C for 425 days. The wood became brittle and darkened in colour when extending the exposure duration at each temperature. At 120 °C, after

1235 days the wood samples gained dark chocolate colour. At 150 °C, after 165 days these wood samples turned into friable charcoal and lost 65 % of weight.

Table 2.1. Loss in weight and transverse shrinkage of hard maple specimens during oven heating (Reprinted from McNaughton, "Ignition and Charring temperatures of wood," Forest Products Laboratory1944)

Duration of heating (days)				Loss of weight (%)	Average transverse shrinkage (%)
At 107 °C	At 120 °C	At 140 °C	At 150 °C		
1050	425	22	16	15	5
	870	58	35	25	9.5
	1235	117	58	35	14.0
		178	88	45	19.5
		320	165	65	32

In 1956, Stamm [6] used kinetic model to characterize the weight loss of wood under different heating conditions for time ranging from 1 minute to 2.4 years in the temperature range from 93.5 °C to 300 °C. Later, Schaffer [18] interpreted the model as:

$$\frac{d\left(\frac{W}{W_0}\right)}{dt} = -k\left(\frac{W}{W_0}\right) \quad (1)$$

where:

W = sample weight at time t

W_0= initial sample weight

k = reaction rate

and $$k = Aexp\left(-\frac{E}{RT}\right) \quad (2)$$

where:

E = Activation energy

A = frequency factor

T= absolute temperature

R = constant of gases

However, Schaffer showed that equation (1) was not precise to construe the thermal degradation of wood over the whole period. According to this equation, at t=t_∞, $W_\infty = 0$ meaning all the wood char would finally be consumed while reality proved that wood was eventually transformed into stable charcoal at low temperature and the final weight of this stable charcoal would keep constant ($W_\infty > 0$). He suggested a more accurate model by Tang [30] where the final weight W_∞ was included to equation (1):

$$\frac{d\left(\frac{W}{W_0}\right)}{dt} = -k\left(\frac{W - W_\infty}{W_0}\right) \qquad (3)$$

Schaffer assumed that cellulosic material must be converted to char before ignition and used 40% residual weight as the indication for the charcoal state of the material. Based on this, he reproduced a graph of 40% residual weight from Stamm's study to roughly forecast the time for wood samples in oven-heated condition to reach ignition (Figure 2.4). He on the other hand stated that: "the study does not confront the question of whether smouldering ignition will eventually occur or not upon reaching this stage". Thus the graph could be interpreted as a prediction of the period of time under a specific low temperature condition to reach fully-charred condition 40 % residual weight.

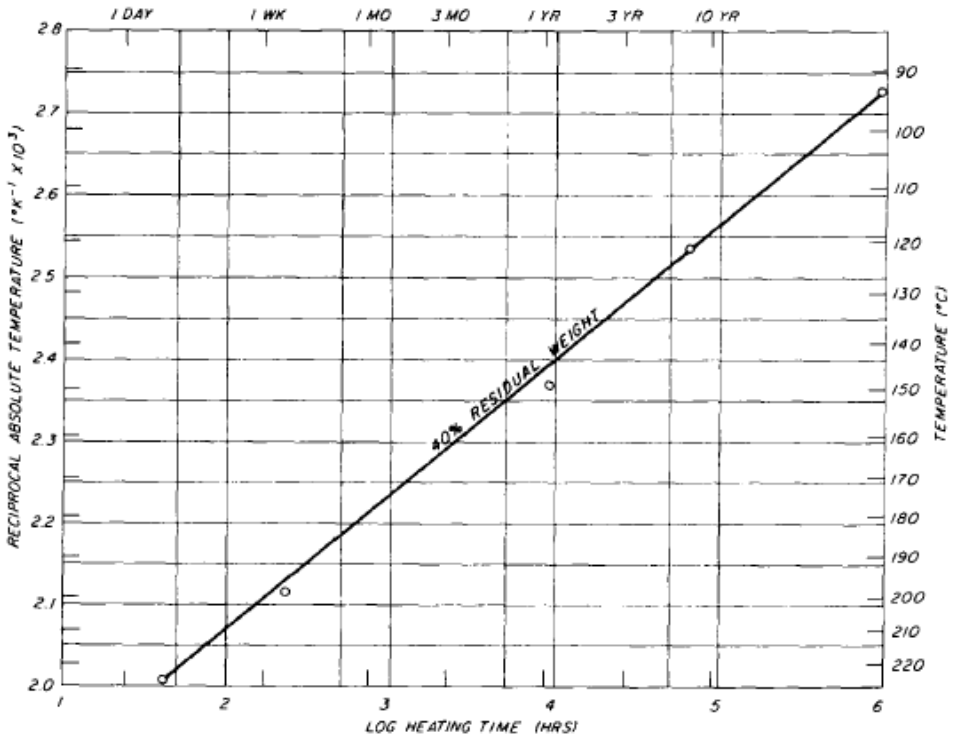


Figure 2.4. The time required to achieve a 40 % residual weight level for oven-heated wood as a function of heating temperature (Reprinted from E. L. Schaffer, "Smouldering Initiation in Cellulosics under Prolonged Low-Level Heating," *Fire technology,* vol. 16, pp. 22-28, 1980)."

2.4. Functional groups and char reactivity

DeGroot and Shafizadeh [7] pointed out that functional groups other than free radicals could play a major role in determining the functionality and reactivity of the char. Previously, Bradbury and Shafizadeh [31] investigated a series of chars prepared by rapid pyrolysis of cellulose in the temperature range of 400-800°C and showed that they had a different chemisorptive affinity for oxygen, maximum oxygen chemisorption appeared around heat treatment temperature of 550 °C where maximum free spin concentration occurred. In this later study by DeGroot and Shafizadeh [7], it was observed that chemisorption of oxygen on chars resulted in a decrease in free radical concentration and heat treatment at 400 °C in flowing

nitrogen restored the original concentration. However, free radical concentrations did not differ significantly between additive treatments over most of the temperature range studied while chemisorption of oxygen did. The study also indicated that the mode of action on inorganic additives in enhancing or inhibiting the solid phase combustion of cellulose chars involved their influence on char functionality development during pyrolysis. It was therefore clear that functional groups are related to the chemisorption characteristics and reactivity of the char.

Calemma et al. [32] investigated coal oxidation at low temperature within 200 °C and 275 °C using FTIR method. They suggested that in this range of temperature, aromatic groups were less reactive than aliphatic groups although aromatic groups did show some modifications leading to less substituted structures during oxidation. The study also showed that different aliphatic groups had different susceptibility towards oxygen: the most susceptible linkages were α-CH_2 groups attached to aromatic rings; CH_3 groups were less reactive and oxidized at harsher conditions.

Furimsky et al. [33] suggested that the active site contained organic groups having a high affinity to oxygen, thus, a high concentration of oxygen chemisorbing groups reflected a high reactivity of carbonaceous solids for oxidation reactions.. At higher temperature, additional groups for oxygen chemisorption were activated, thus, there was an increase in oxygen chemisorption. However, in contrast to previous study by Calemma et al., they proposed that benzylic and hydro-aromatic groups were the most reactive groups.

Recently, Hshieh and Richard [34] have done an investigation of possible chemical effects involved in the chemisorption activity peaks of wood chars prepared at charring temperatures of 375 °C, 475 °C and 575 °C and held for 10 minutes in flowing nitrogen in a pyrolysis furnace. The chemisorption temperature of the wood

char was chosen at 140 °C. Following Furimsky et al. [33], they proposed that groups like benzylic CH and structures such as 9-10-substituted anthracenes were especially reactive and the reactions of benzylic groups with oxygen were likely to progress to form a carbonyl group which explained the increase in the band at 1700 cm^{-1} due to chemisorption.

2.5. Oxygen Chemisorption

2.5.1. Oxygen chemisorption and char reactivity

According to Shafizadeh et al.' studies [7, 19, 25, 31], oxygen chemisorption on carbonized cellulose initiated the gasification process through the formation of ultimate gaseous combustion products. The heat flux from chemisorption played an important role in controlling the chemical reactivity and solid phase ignition of cellulosic materials at low temperatures.

It was essential to differentiate between chemisorption and physical adsorption of oxygen [35]. Chemisorption is a type of adsorption in which a substance is strongly bound onto the surface of another substance. Physical adsorption is characterized by the binding of substances through intermolecular forces which are rather weak and similar to the forces responsible for condensation process. Physical interactions are different from chemical interaction in general, thus, physical adsorption owns different features comparing to chemisorption. Physical adsorption can occur in any gas/solid system, for example wood char can absorb nitrogen physically but it could not react chemically. With the weak interaction between the substances, the absorbed gas molecules easily leave the solid surfaces [35] while in chemisorption, after chemical reactions, the original substances may not be recovered through desorption. The elementary step in physical adsorption of a gas on a solid does not

involve activation energy like in chemisorption. Under appropriate conditions of pressure and temperature, physical adsorption may result in multiple layers of adsorbed molecules rather than single layer which are in direct contact with the surface, while chemisorptions is limited to a monolayer on the surface only.

2.5.2. Elovich equation:

Elovich equation has been widely used to interpret the rate of chemisorption of a gas by a solid:

$$\frac{dw}{dt} = a\ exp(-bw) \qquad (4)$$

where:

w = weight of gas absorbed at time t

a, b = Elovich constant

According to McLintock[36], the equation was first proposed by Roginsky and Zeldovich, previously it was also called as “Ronginsky-Zeldovich”, “Zeldovich-Roginsky” or “Elovitz” [37].

Beside Elovich kinetic model, Langmuir model for adsorption has also been used to illustrate the oxygen chemisorption of carbon. However, the use of this model has some drawbacks: the assumptions of this model include all adsorption sites are equally active and the energy of an adsorbed particle is the same at any site on the surface and is independent of the presence or absence of nearby adsorbed molecules; but these assumptions do not satisfy experimentally, each specific site should have different activity and interactions do exists [38]. Comparing with Langmuir model, Elovich model fits experimental data better. Although Elovich

equation received criticisms from some researchers like Laidler [39] and Gray [40], Taylor and Thon [41] have proved mathematically that the Elovich equation had generally widespread utility with precision in reproducing data of chemisorption kinetics[41][41][41][41][43][43][42][41][38]. The equation satisfactorily covered a large range of the course of the slow adsorption and failed mostly only towards the end of the reaction where the process becomes excessively slow as stated by Low [37]. When applied to an adsorption system, Elovich equation provided a convenient method of graphing and interpolating the chemisorption data; besides, it allowed calculation of instantaneous rates of adsorption [42]. The explanation for Elovich kinetic law involved a variation of the energetic of chemisorption with the extent of coverage. The heterogeneous nature of the active sites was another probable explanation, thus these sites displayed different activation energy for chemisorption [43].

Many researchers used the thermo-gravimetric analyzer (TGA) for oxygen absorption testing and Elovich equation for interpretation of chemisorption process of different cellulosic materials created at different conditions. Alladice [42] applied Elovich equation for study on the absorption of oxygen at pressures up to one atmosphere and temperatures from 25 °C to 200 °C on brown coal char carbonized at 1000 °C. Shafizadeh et al. [7, 31] applied this equation for the chemisorption of reactive cellulosic chars created at 550 °C for 1.5 min at several isothermal chemisorption temperatures ranging from 74 °C to 207 °C. Teng and Hsieh observed that oxygen chemisorption process of resin char treated at 900 °C also followed Elovich kinetic law [43]. Recently, Floess et al. [44] also found the chemisorption data of micro-porous char fitted well with Elovich equation.

2.6. Concluding remarks

In this chapter, extensive literature was reflected to provide an overview about pyrolysis, self ignition and self heating of wood materials. There was almost an agreement among researchers that wood generated charcoal after heating at low temperature for long durations and thus might lead to fire breakouts due to self ignition. However, there was still incomplete information on the pyrolysis of wood materials until reaching the charcoal state. In addition, the self ignition fire incidents were relied on observations without experimental proofs on the reactivity characteristics of the long-term low-temperature wood chars. As it was discussed, the reactivity characteristics of the chars could be reflected through the functional groups and chemisorption properties. The review indicated the need for more focused research in which the methodological approach would be explained in details in the next chapter of this study.

CHAPTER 3

Research Methodology

3.1. Introduction

This chapter described the research methodology to investigate the pyrolysis process and characterization of wood chars. Firstly, the selection of materials was discussed with the details of the wood species. This was followed by the description of pyrolysis experiments in ovens; explanations for the chosen heat treatment temperatures, durations and oxygen conditions were also provided. Then, the two analytical methods used to evaluate char reactivity were described. Each technique attempted to provide objective and repeatable results for the characteristics of pyrolyzed chars. FTIR was employed to measure the functionality as it is useful for identification of functional groups presenting in the molecules. Using FTIR, the changes in functional groups during experimental process can be reviewed. TGA was employed to quantify oxygen chemisorption.

3.2. Selection of materials

Kapor (Dryobalanops) and Nyatoh (Palaquium) wood were selected as the raw material for the present study. These two are among the most common tropical moderate hardwood species found in Southeast Asia. The mean densities of Kapor wood and Nyatoh wood are 0.74 g/cm^3 and 0.57 g/cm^3 respectively at 12% moisture content, 1 MPa. Both types of wood have very wide application in daily

life. In construction, they are mainly used for structural components (columns, beams, joists and girders) or non-structural components such as floors, roofs and staircases. In addition, Kapor and Nyatoh wood are popular materials for furniture and interior decorative finishing of buildings like joinery, lining, etc. These wood species are also used for other purposes like packing cases for storage of goods and boat building.

3.3. Pyrolysis experiments

Small block specimens were prepared at size of 1 ¼ x 1 ¼ x 4 inches as illustrated in Figure 3.1. To ensure the consistent behaviour of wood samples during heat treatment, all wood specimens were taken from the same wood source and each had the same grain orientation. These wood blocks were then stored in a dry cabinet at temperature 24 °C and humidity 45% for several days prior to heat treatment.

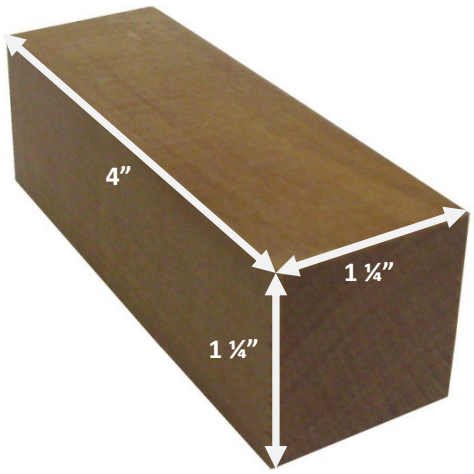


Figure 3.1. Fresh wood block size 1 ¼ x 1 ¼ x 4 inches.

The specimens were heated isothermally at low temperatures (160 °C, 175 °C and 190 °C) for extended duration up to 153 days (5 months) in order to simulate self heating conditions. Temperatures within the range 160-190 °C were chosen because many lignocelluloses materials have been subjected to such temperatures before self ignition happened, self-heating had been observed to be evident at temperature about 160 °C [45]. The pyrolysis experiments were carried out in both air and vacuum. The weight loss of each specimen versus time was recorded. The specific heating condition for each sample together with it weight loss after heat treatment is described in Table 3.1.

3.3.1. Heat treatment in atmospheric condition

In atmospheric condition, experiments were conducted at 160 °C, 175 °C and 190 °C in Carbolite oven (Figure 3.2) for extended duration from 12 days to 153 days (5 months) as shown in Figure 3.3. The oven temperature was maintained constant except when the oven door was opened.

Figure 3.2. Cabolite oven.

Figure 3.3. Wood specimens heated in Cabolite oven with access of air.

3.3.2. Heat treatment in vacuum condition

Figure 3.4. Vacuum oven with vacuum pump.

In vacuum condition, the specimens were heated at 175°C for 12 days and 26 days in vacuum oven (Figure 3.4). These blocks were cooled down to room temperature before taking out to prevent the newly formed char to be in contact and react with oxygen at high temperature. At room temperature, the oxidative layer formed by oxidation reaction was insignificant.

Table 3.1. Heat treatment conditions and weight loss of wood char specimens

Heat treatment conditions			Weight loss (%)	
Environment	**Temperature (°C)**	**Duration (days)**	**Kapor**	**Nyatoh**
Air	160	19	20.6	22.8
		31	25.0	27.1
		45	30.2	32.1
		60	36.1	38.7
		87	46.4	46.7
		112	53.5	53.1
		153	59.8	60.9
	175	12	27.5	24.7
		26	34.8	41.0
		41	44.6	52.9
		68	56.4	62.3
		93	64.3	65.4
	190	0.18	11.7	11.7
		1	15.1	18.1
		3	17.7	27.1
		8	21.3	41.4
		13.5	25.4	53.1
		16	30.5	60.7
		22	39.5	65.6
		29	49.7	67.7
		36	57.3	70.0
Vacuum	175	12	17.5	22.2
		26	20.9	30.9

3.4. Fourier Transform Infrared Spectroscopy

3.4.1. Basic principles

FTIR detects the energy absorption corresponding to the molecular vibration when the molecule is irradiated with electromagnetic radiation. The amount of energy that a molecule can contain is quantized or in other words the molecule can only vibrate at specific frequencies. By interpreting the frequencies of the vibration modes, the bonds (functional groups) presenting in the molecule can be found [46]. This can be done by using spectra correlation tables which indicate one or more absorption bands in a given infrared spectrum to the vibrational modes associated with a certain functional group [47]. The intensity of the absorption band is determined by the value of the change in the dipole moment for the given type of vibration; the larger the change in the dipole moment, the stronger the absorption bands [48].

In a conventional spectrometer, dispersion property of either a prism or a diffraction grating is applied. The prism or grating will separate the individual frequencies of the energy emitted from the infrared source. Fourier-transform infrared spectroscopy (FTIR) uses an interferometer in place of the prism or grating, the interferometer produces a unique type of signal which has all of the infrared frequencies. Nowadays, FTIR is more preferred comparing to the conventional dispersive spectrometer due to its obvious performance advantages. FTIR provides multiplex (Fellgett's advantage) and throughput (Jacquinot's advantage) over dispersive methods: all the resolution elements are measured continuously and simultaneously and greater amount of radiation can be passed between the source and the detector for each resolution element [47]. In addition, the instrument is

mechanically simpler with less likeliness to damages and it can self-calibrate thus providing more accuracy and precision.

In this study, FTIR technique was used to identify the presence or absence of functional groups to characterize the resulted wood chars.

Solid samples are normally ground and mixed with potassium bromide (KBr) then pressed into pellets for the ease of measurement. KBr is transparent from the near ultra violet to the long wave infrared wavelengths so it will not affect spectral results of the samples. For chemical analysis, the spectra are often measured in the mid-infrared range (4000 cm^{-1} to 400 cm^{-1}) which shows the changes in vibrational energies within molecules.

The spectra can be displayed as percentage of transmittance T or absorbance A versus wave-number ν $(1/\lambda)$ cm^{-1}. In this study, absorbance versus wave-number was used for all spectral plots.

3.4.2. Experimental procedures

Infrared spectra were measured on IR Prestige-21 Spectrometer (Figure 3.5) with DLATGS detector. All spectra were recorded in the range between 4000 cm^{-1} and 400 cm^{-1}, resolution of 8 cm^{-1} and repetition of 32 scans. To prepare for FTIR experiments, all wood char blocks were ground and sieved into fine powder. The char powder was then measured in potassium bromide (KBr) pellets. Each pellet was prepared by adding 1.3 mg wood char powder to 300 mg KBr. This proportion had been proved to produce optimum results for most chars [49]. All pellets were compressed in the same manner with a hydraulic laboratory hand press (Figure 3.6.a) of 10-ton capacity. The potassium bromide pellets (Figure 3.6.b) were dried

under vacuum at 60°C overnight in order to remove absorbed moisture. All spectra were smoothed and baseline corrected, all comparisons were made qualitatively.

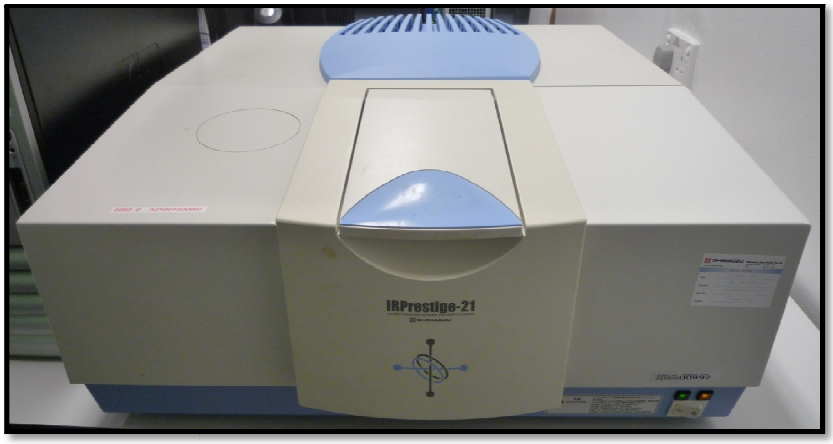


Figure 3.5. IR Prestige-21 Spectrometer

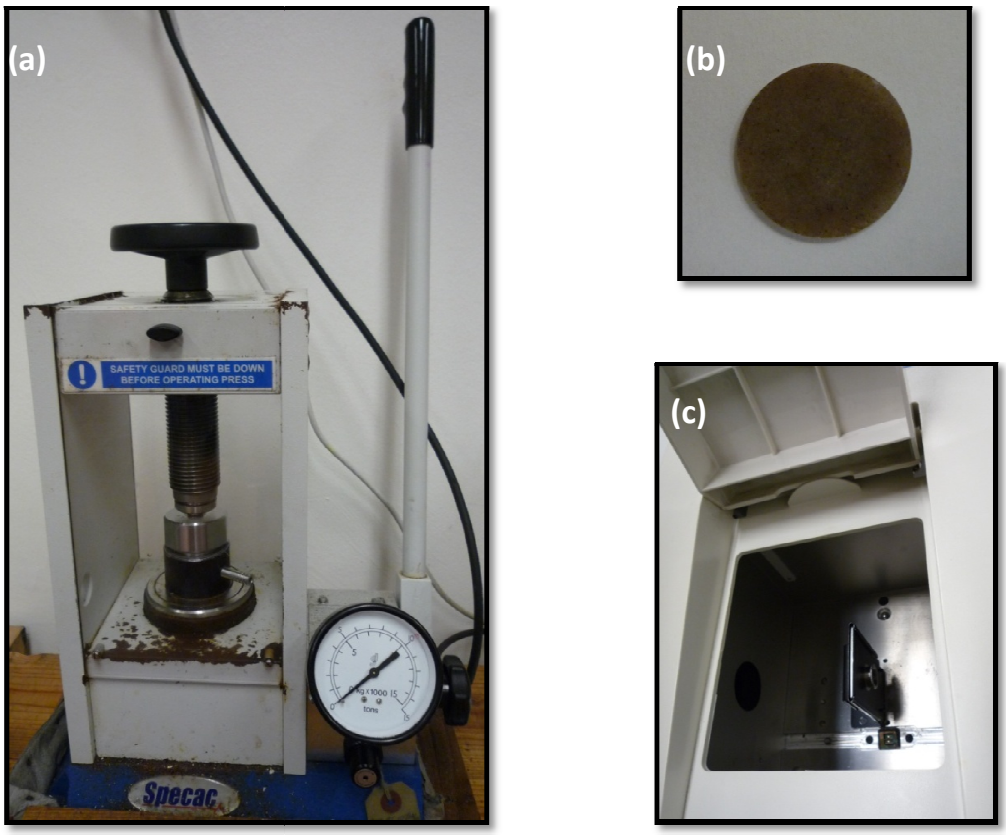


Figure 3.6. FTIR equipment: (a) Hydraulic laboratory hand press to produce pellet, (b) pellet of char powder and KBr, (c) pellet held in plate for measurement inside the spectrometer.

3.5. Thermo-gravimetric Analysis

3.5.1. Basic principles

TGA is an analytical technique that monitors the weight change (loss or gain) of a sample as a function of time or temperature through a thermo-balance when the sample is heated. At a specific temperature, the sample weight change corresponds to the following process: volatilization of sample components, decomposition, oxidation or other changes. The thermo-balance consists of an electronic microbalance connected to a furnace, a temperature control and a computer. When the sample is heated inside the furnace, the sample weight changes, this will lead to the imbalance status, a force coil will detects this and produces additional electromagnetic force to recover equilibrium; this additional electromagnetic force is proportional to the mass change. Normally, the measurements are carried out at a controlled atmosphere: air (oxidative) or nitrogen (non-oxidative). In this study, chemisorption experiments were performed at isothermal temperatures, thus each sample was heated to the desire temperature and the weight of the sample is measured throughout the experimental period.

There are two types of TGA apparatuses: vertical and horizontal balance. Due to equipment availability, in this study, horizontal balance apparatus is used (SDT 2960) (Figure 3.7), it has two pans: one sample pan and one reference pan (Figure 3.8).

3.5.2. Experimental procedures

SDT 2960 simultaneous DTA-TGA (Figure 3.7) was used as TGA apparatus; it has 0.1 microgram scale sensitivity. Experiments were performed under air flow of 60 ml/min and nitrogen flow of 100 ml/min. 10 mg of char was placed in a sample pan suspended from the balance beam in TGA instrument.

Oxygen chemisorption measurements were performed on Kapor aerobic chars preheated at 175°C for 26 days and 93 days and Kapor anaerobic chars preheated at 175°C for 26 days. The experimental procedure was as followed: the preheated char was reheated to 175°C at 20°C/min in nitrogen and held at that temperature for 8 hours to reactivate the surface after storage. The sample was then cooled to CST (chemisorption temperature) and maintained at this temperature until no further weight loss was observed. A run was started by switching from nitrogen to air. According to Bradbury and Shafizadeh [31], the affinity for physical adsorption of nitrogen and oxygen gas were similar at temperature up to 80 °C. In this study, similar affinity for adsorption of nitrogen and air was found, thus, equilibration of air and nitrogen did not affect the weight due to physical absorption when switching from nitrogen gas to air. CSTs were chosen at below 70°C as rate of thermal decomposition of oxygenated complexes was accelerated at oxidation temperature exceeding 70°C [50]. The experiments were carried out for 420-720 min (7-12 hours).

Figure 3.7. TGA apparatus SDT 2960

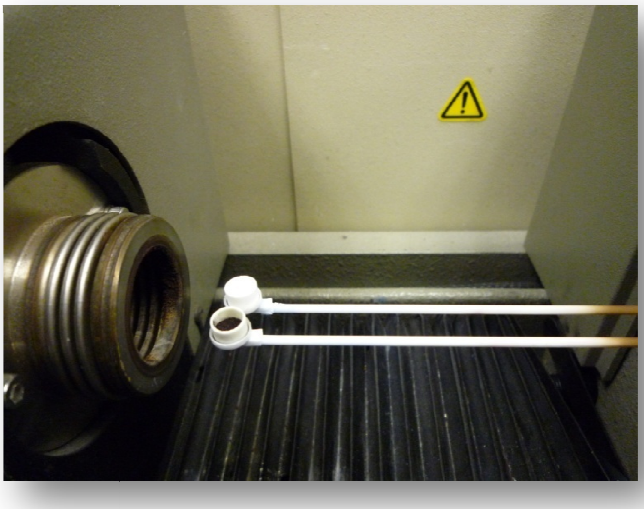


Figure 3.8. Aluminium sample pan holding wood char and empty reference pan on balance beams of SDT 2960

3.6. Concluding remarks

In this chapter the methodological approach for the study was discussed. In addition, proper issues that were taken care of when carrying out the experiments were outlined. The wood chars were first created from pyrolysis experiments in ovens. These pyrolyzed chars were then analyzed using FTIR and TGA analytical methods. The experimental data gathered would be presented and discussed in Chapter 4 and Chapter 5.

CHAPTER 4

Pyrolysis of wood

4.1. Introduction

This chapter discussed and analysed the data collected from the pyrolysis experiments of Kapor and Nyatoh wood samples. The first part described the physical appearance and weight changes of the wood blocks during heat treatment periods in both aerobic and anaerobic conditions. The next part on elemental analysis showed the chemical transformation in wood chars through the changes in percentage of individual components. This was followed by the kinetic study of wood pyrolysis. An empirical model of the pyrolysis of wood was built based on the weight loss of the wood chars. The chapter concluded with the main findings on wood pyrolysis based on the experimental results.

4.2. Descriptions of heated wood chars

The weight of each wood block was recorded during the process of prolonged heating. There was significant reduction in weight at the end of heat treatment process indicating the destruction in chemical structure. Table 3.1 in Chapter 3 summarized the weight loss of all Kapor and Nyatoh wood specimens at different heating duration. The rate of weight loss was observed to be fast initially and slowed down as heating duration increased. Some visible characteristics like the

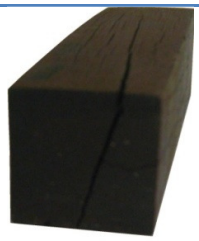
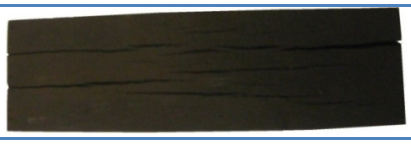
change in colour, shrinkage and the appearance of cracks was observed. The degree of transformation in colour, shrinkage and cracks depended on the exposed temperature and duration of heating. Ignition did not happen to all the specimens during the heat exposure.

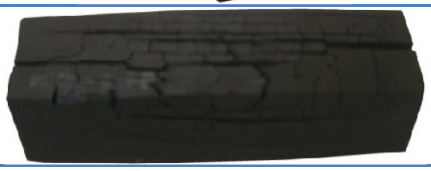
Table 4.1 presented the visual description of Kapor wood blocks heated in air at 160 °C and 175 °C. Those heated at 190 °C had very similar changes. At each isothermal temperature, the wood colour gradually changed from yellow brown to darker colour and eventually to black colour of charcoal. Transverse shrinkage happened. Cracks and fissures appeared on the wood surface, beginning with some hairline cracks and progressively developed into wider cracks and cross-grained fissures. The wood block lost 60% in weight after 153 days (5 months) at 160 °C and 65% after 93 days (3 months) at 175°C. Before this, the wood blocks already became fragile and turned into well-burnt charcoal (after 87 days at 160°C, 44 days at 175°C and 22 days at 190 °C).

Nyatoh wood blocks also took the same development in colour, cracks and shrinkage as displayed in Table 4.2. The crack pattern and degree of shrinkage were different with Kapor wood due to the different in species, density, physical and chemical structure. Nyatoh wood specimens were observed to have less cracks and more shrinkage than Kapor wood. The specimens became much bristle with prolonged heat exposure; after 93 days at 175 °C the specimens were so fragile that they broke into small pieces. Nyatoh wood also showed faster rate of weight loss at higher temperatures. At 190 °C, after 16 days, Nyatoh wood specimens lost nearly 61% of weight while Kapor wood specimens only lost around 30% of weight.

McNaughton [5] showed similar thermal behaviour of wood in some tests at the Forest Products Laboratory. The wood specimens of size 1 1/8 x 1 ¼ x 3 inches were heated isothermally at different low temperatures in the range from 107 °C to 150 °C for various extended durations in electrical controlled drying ovens. During the heat exposure, the specimens also showed the darkening in colour, the shrinkage in size and the cracks on the surface and the appearance of friability of charcoal after very long heating duration. They lost 65% of weight after heating at 150°C for 165 days and 140°C for 320 days.

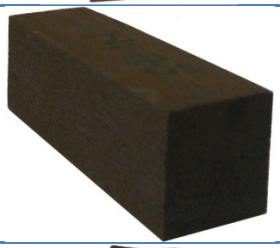
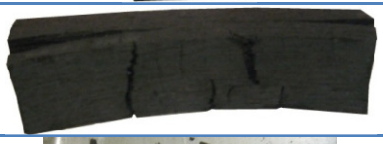
Table 4.1. Description of Kapor wood specimens after heat treatment at 160°C and 175°C in air.

Duration	Picture	Descriptions
Kapor at 160 °C in air		
Untreated		Yellow brown colour
21 days		Brown colour No crack appeared Little shrinkage
31 days		Brown colour Hair-line cracks along the longitudinal grain More shrinkage
45 days		Dark-brown colour Wider cracks along the longitudinal grain

60 days		Darker-brown colour Wider cracks along the longitudinal grain Appearance of cross-grain fissures
87 days		Black colour Longitudinally-oriented cracks intersected cross-grain fissures
110 days		Black colour Very wide longitudinal cracks
153 days		Black colour Very well-burnt char with a lot of cracks and fissure Fragile chars (broke when touched)
Kapor at 175 °C in air		
12 days		Dark brown colour Shrinkage Longitudinal cracks Some hair-line cross-grain fissures
26 days		Darker brown colour Wide cracks and fissures
41 days		Black colour More shrinkage Wider cracks and fissures

68 days		Black colour Turned into char (fragile), some small pieces broke from the block
93 days		Black colour Very well-burnt char with a lot of cracks and fissures Very fragile (broke when touched)

Table 4.2. Description of Nyatoh wood specimens after heat treatment at 175°C in air.

Name	Picture	Descriptions
Nyatoh at 175 °C in air		
Untreated		Yellow brown colour
12 days		Dark brown colour Shrinkage
26 days		Very dark brown colour Further shrinkage Cross-grain cracks
41 days		Black colour Further shrinkage and bending Longitudinal cracks Turned into char (fragile)
67 days		Black colour Well-burnt char (fragile) More cracks
93 days		Black colour Extremely fragile (broke when touched)

Comparing with wood specimens heated in air, those heated in vacuum degraded less. Kapor wood blocks lost around 17.5 % and 21% in weight after 12 days and 26 days at 175°C, much smaller than those treated in air (27.5% and 35% respectively) at the same temperature and duration conditions. Figure 4.1 showed the picture of these Kapor vacuum-treated wood blocks. Only some small cracks appeared on transverse surface after 26 days. There were no severe longitudinal crack and cross-grained fissure like air-treated samples. These differences could be explained by the lack of oxidative degradation of the wood specimens in vacuum condition. Nyatoh wood blocks heated in vacuum condition also gave similar result.

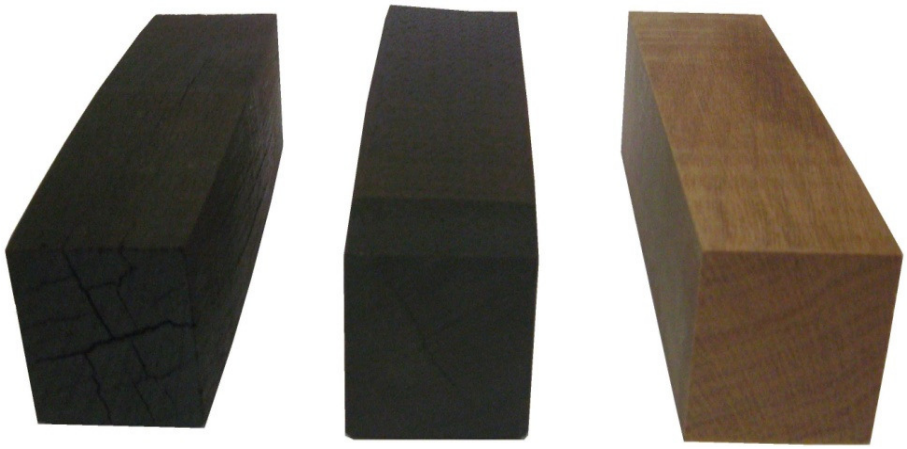


Figure 4.1. Kapor wood specimens after heat treatment in vacuum for duration of (a) untreated, (b) 12 days, (c) 26 days.

4.3. Elemental analysis

Table 4.3. Elemental analysis of Kapor wood chars after heat treatment at 160 °C and 175 °C.

Environment	HTT (°C)	Duration (days)	Char Name	Composition (% weight)			Empirical formula (ref. to
				C	H	O	
Air	No treatment		KF	46.2	6.19	47.53	$C_6H_{9.6}O_{4.6}$
	160	21	A-160-21	48.3	5.21	46.42	$C_6H_{7.8}O_{4.3}$
		45	A-160-45	49.8	4.78	45.33	$C_6H_{6.9}O_{4.1}$
		87	A-160-88	52.9	3.62	43.47	$C_6H_{4.9}O_{3.7}$
		112	A-160-110	53.7	3.44	42.77	$C_6H_{4.6}O_{3.58}$
		153	A-160-152	53.7	3.19	43.08	$C_6H_{4.3}O_{3.61}$
	175	12	A-175-12	53.6	3.83	42.48	$C_6H_{5.1}O_{3.6}$
		26	A-175-26	53.0	3.73	43.18	$C_6H_{5.1}O_{3.66}$
		41	A-175-41	53.2	3.52	43.21	$C_6H_{4.8}O_{3.65}$
		68	A-175-69	53.4	3.05	43.54	$C_6H_{4.1}O_{3.67}$
		93	A-175-91	54.6	2.81	42.59	$C_6H_{3.7}O_{3.5}$
Vacuum	175	12	V-175-12	50.4	5.76	43.75	$C_6H_{8.2}O_{3.9}$
		26	V-175-26	52.4	5.75	41.83	$C_6H_{7.9}O_{3.6}$

Table 4.3 provided the elemental analysis of wood chars after thermal treatment at different conditions. At each isothermal temperature, the percentage of each element varied with time indicating chemical transformation happening to the chars. Carbon content of thermal treated wood chars increased as HTT (heat treatment temperature) and heating duration increased. The increase of the carbon content and decrease of hydrogen and oxygen content revealed the loss of functional groups containing predominantly oxygen and hydrogen like hydroxyl groups and the condensation of aromatic structures. These characteristics were also reflected in signal of infrared spectra. Furthermore, for samples heated in air, there were differences in the reduction of carbon content and the other two elements in residues as shown in Figure 4.2. The rate of decrease of hydrogen and oxygen was faster in the initial period and slowed down as the degradation course proceeded. In the opposite, the rate of carbon content reduction was slower at first and got faster

afterward. These differences signified the contribution of dehydration reaction to weight loss at the beginning of heating treatment [51].

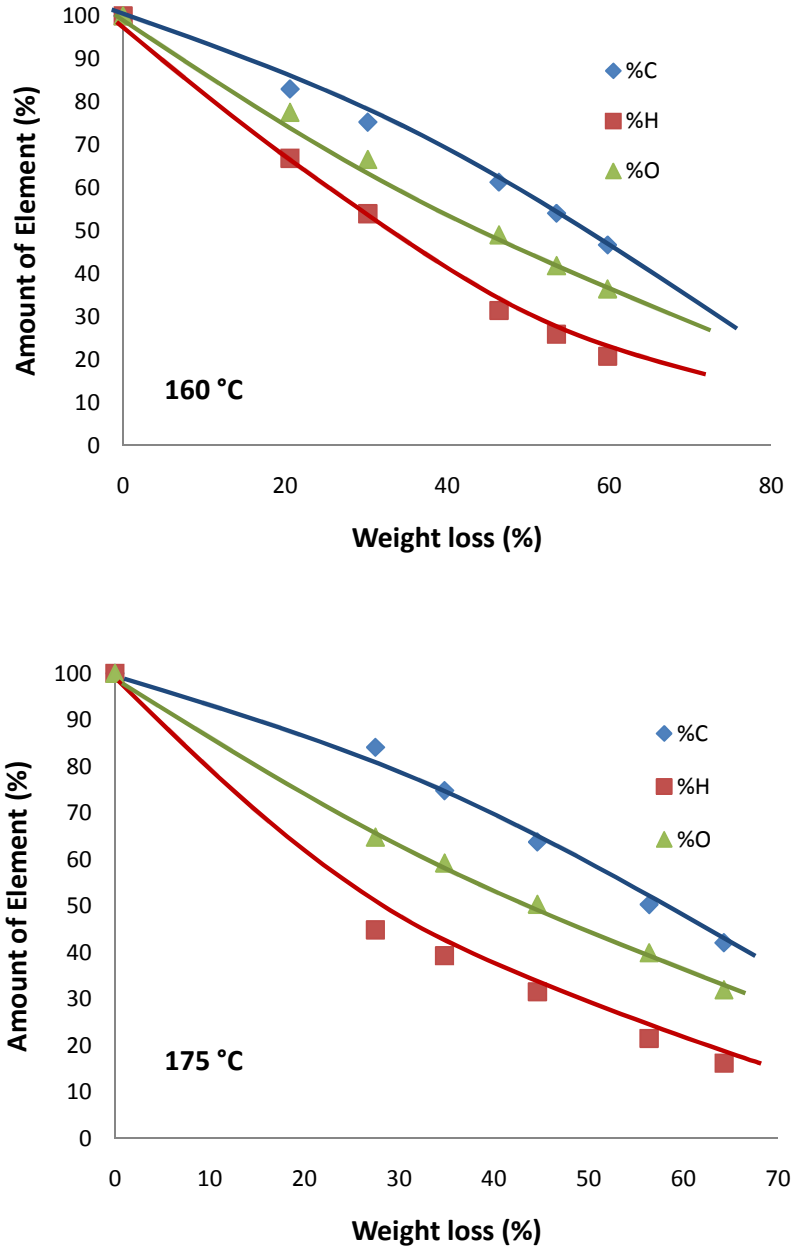


Figure 4.2. Plots of percentage of elemental content in char residues versus weight loss of Kapor wood specimens heated in air at 160°C and 175°C.

4.4. Kinetics of pyrolysis of wood specimens in air

Weight-loss data for the pyrolysis of wood specimens in air at different isothermal temperature conditions were shown in Figure 4.3. At the beginning, the rate of weight loss was faster; this might be explained by the dehydration of water content inside the wood specimens which corresponded to the trend of elemental weight loss as described in Figure 4.2. The rate of weight loss decreased gradually with time until the point when wood was transformed into stable charcoal and kept the final weight constant. To reach this final stage, it might take many years and it was unrealistic to continue the experiments till the end. Thus, to find the final weight, graphic extrapolation was applied following the method used by Dollimore [52], Fairbridge [53, 54] and Herrera [55]. The value of W_∞/W_0 was determined by drawing a plot of weight loss $(W_0 - W/W_0)$ against reciprocal of time (1/t). When t got large, 1/t became small, the graph became linear. At t=t_∞, $1/t_\infty$= 0, weight loss equalled to $[(W_0 - W_\infty)/W_0]$, this point was the intercept of the linear line with the $(W_0 - W/W_0)$ axis. Final weight of the Kapor and Nyatoh wood heated in air at 160°C, 175°C and 190°C were in the range of 19-25% (Table 4.4). These values were slightly smaller than those final remaining weight 25-30 % found by Reina [56] and Ward [57] obtained from forest waste and hardwood in a thermo-gravimetric study and an isothermal tube furnace respectively.

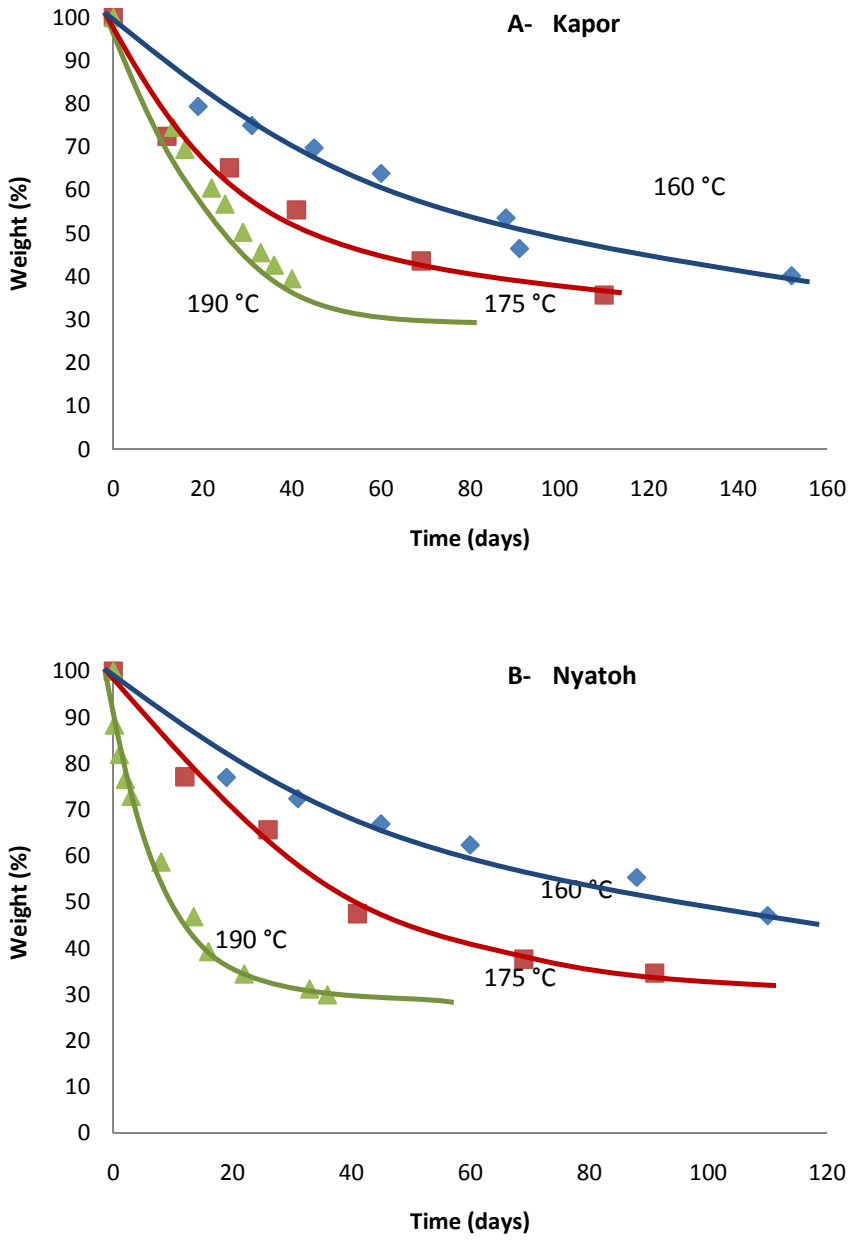


Figure 4.3. Plots of percentage of residual weight of wood specimens under isothermal heating in air: A- Kapor wood, B- Nyatoh wood.

The kinetics of weight loss of wood followed the equation:

$$-\frac{d\left(\frac{W}{W_0}\right)}{dt} = k\left(\frac{W - W_\infty}{W_0}\right)^n \quad (1)$$

where:

k = kinetic constant

n = reaction order

t = time (day)

W_0 = weight of the sample at time 0

W = weight of the sample at time t

W_∞ = final weight of the sample at time t_∞

Equation (1) was also written as:

$$\frac{d\left(\frac{W_0 - W}{W_0}\right)}{dt} = k\left(\frac{W - W_\infty}{W_0}\right)^n \quad (2)$$

The kinetic constant,k was expressed according to the Arrhenius equation in which:

$$k = Aexp\left(-\frac{E}{RT}\right) \quad (3)$$

where:

A = preexponential factor

E = Activation energy (kJ/mol)

R = constant of gases (=8.314 J/mol.K)

T = absolute temperature (°K)

Assuming first-order reaction (n=1), upon integration and linearization with initial condition $t=t_i$ and $W=W_i$ equation (2) became:

$$\ln\left(\frac{W - W_\infty}{W_0}\right) = \ln\left(\frac{W_i - W_\infty}{W_0}\right) + kt_i - kt \qquad (4)$$

The value of k could be obtained by plotting $\ln\left(\frac{W-W_\infty}{W_0}\right)$ against t. As shown in Figure 4.4, the plots resulted in a straight line at each oven heating temperature confirming first-order reaction which was assumed earlier. The first order reaction (with n equal to 1) obtained here was in good agreement with many other studies on thermal degradation of lignocellulosic materials of Stamm [6], Tang [30], Brink [58] and Reina et al. [56]. However, most of the straight linear lines did not pass through the origin; this showed that the initial mass loss was another part to the later first order process. This initial mass loss was very fast with the attribution of water content dehydration. Table 4.4 showed the values kinetics constant k of Kapor and Nyatoh wood at different temperatures during the first order process. For both wood, k increased as temperature increases, this agreed with equation (2) since $\frac{d\left(\frac{W_0-W}{W_0}\right)}{dt}$ values increased with temperature while final weight W_∞ did not vary greatly with the change in temperature.

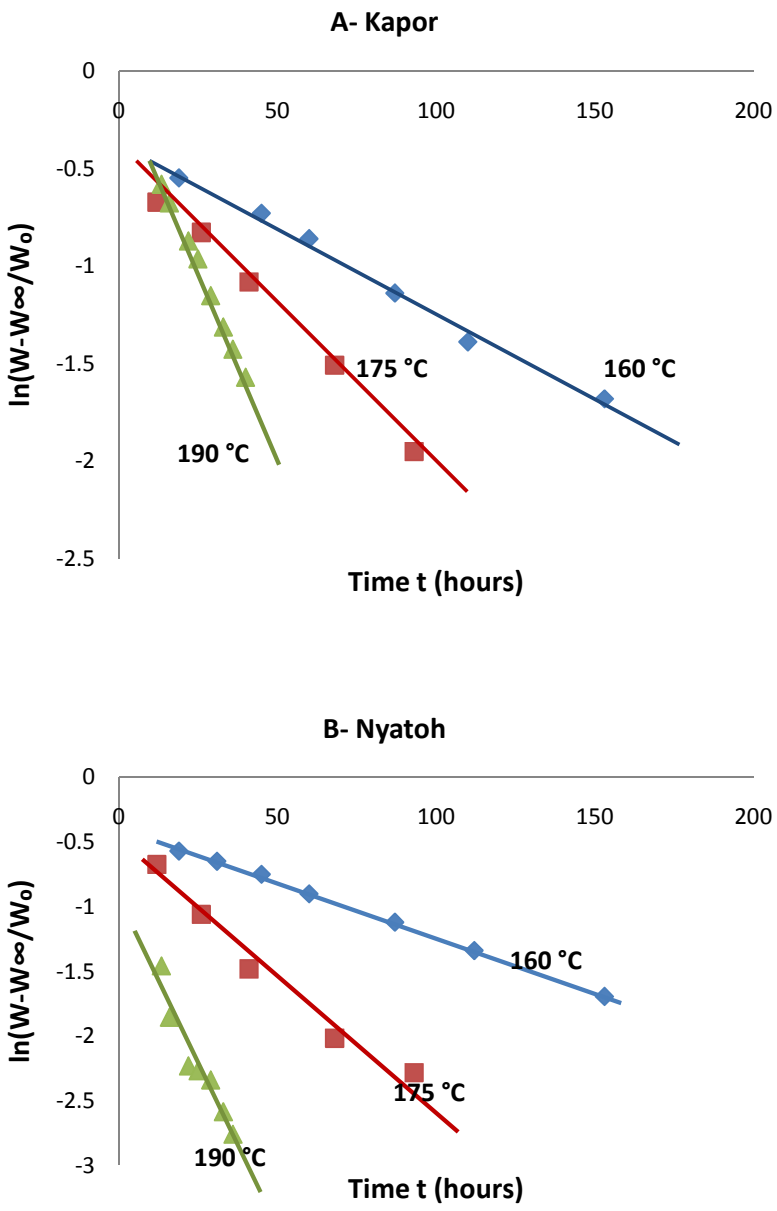


Figure 4.4. Plots of ln $\left(\frac{W-W_\infty}{W_0}\right)$ versus time of A-Kapor and B-Nyatoh wood heated in air.

Table 4.4. Values of final weight residue and constant k when heating wood specimens at low temperatures (Refer to Appendix 1 and 2).

KAPOR			
Temperature	160 °C	175 °C	190 °C
Final weight $\frac{W_\infty}{W_0}$ (%)	21.58	21.47	18.68
k (day^{-1})	0.0088	0.016	0.0377
NYATOH			
Temperature	160 °C	175 °C	190 °C
Final weight $\frac{W_\infty}{W_0}$ (%)	20.74	24.4	23.67
k (day^{-1})	0.0085	0.02	0.0542

From equation (3), activation energies were found by plotting ln(k) versus the reciprocals of absolute temperatures as shown in Figure 4.5. The slopes were calculated by linear regression. It could be seen that in the low temperature range 160°C to 190°C activation energy of Kapor wood was 77.5 kJ/mol (18.52 kcal/mol) and Nyatoh wood was 102.8 kJ/mol (24.6 kcal/mol), these values were still within the reported range in literature[59] between 54 kJ/mol and 174 kJ/mol. However, they were slightly lower than the value 29.5 kcal/mol reported by Stamm [6] for softwood in the temperature range 93.5-250°C. In fact, there were differences in the reported results by different researchers. Thuner and Mann [60] found activation energy of oak wood at temperature range 300-400 °C equalled to 106.5 kJ/mol, Browne and Tang [61] found activation energy of wood heated in the range 110-600 °C equalled to 149.6 kJ/mol while Brink [58] found the activation energy for wood sawdust in temperature range below 650 °C equalled to 58.5 kJ/mol. The differences between the studies could be attributed by the differences in experimental equipment, experimental methodology, experimental conditions, kinetics model, physical properties (size) and chemical composition of the materials (due to difference in species).

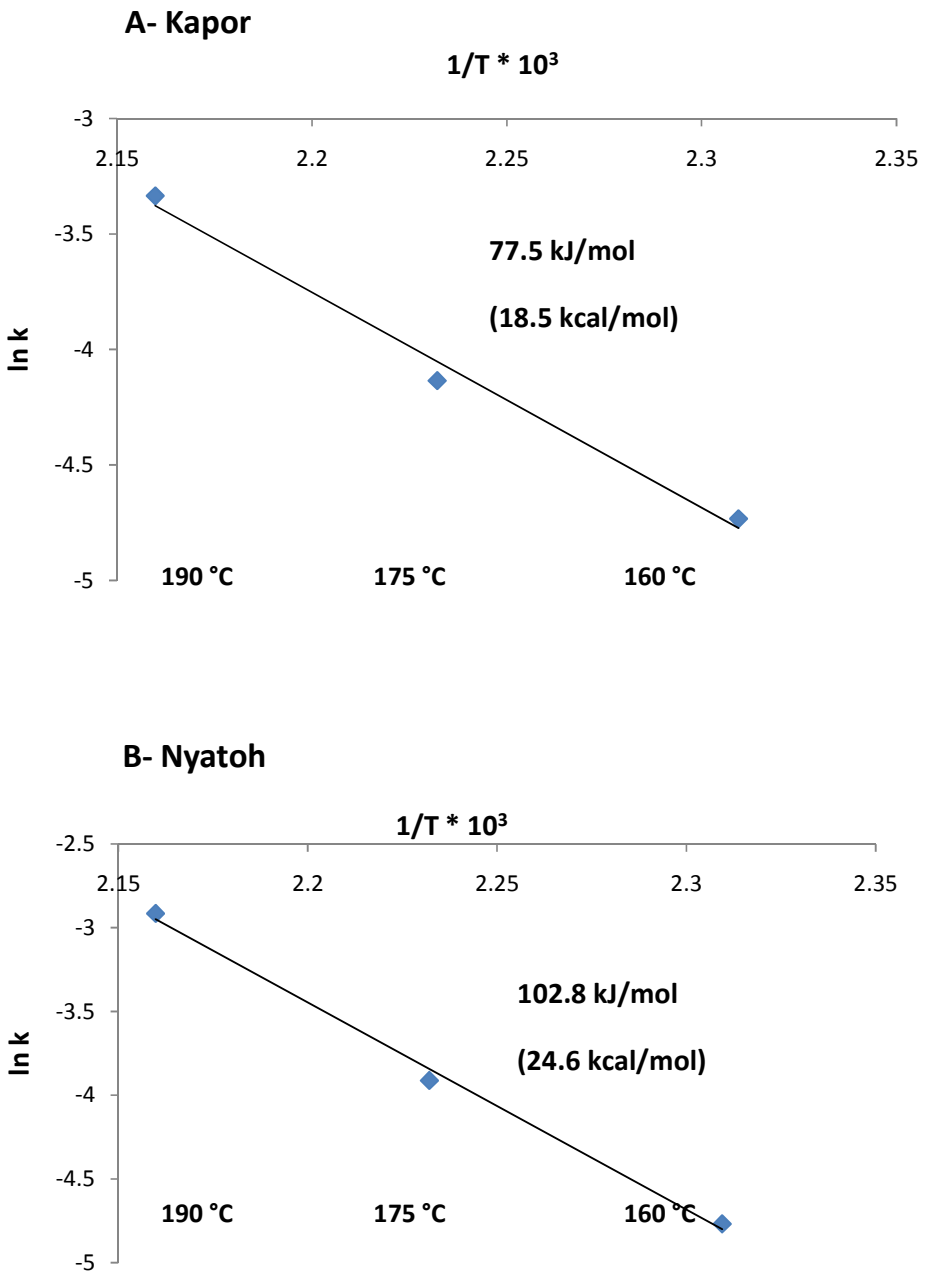
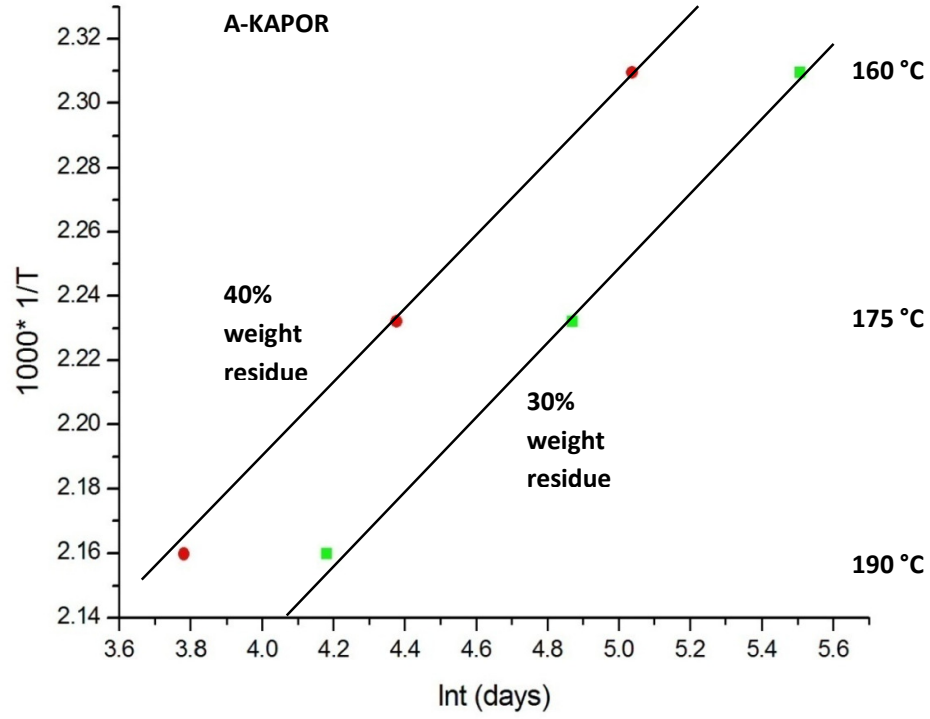


Figure 4.5. Plots of $\ln k$ versus reciprocals of absolute temperature of: A-Kapor and B- Nyatoh wood.

The percentage of final weight of Kapor and Nyatoh wood did not vary much when heated at 160°C- 190°C in air, thus it was assumed that the final weight of these two types of wood was approximately 22% which was the average value of final weight obtained by graphic extrapolation method. This was in agreement with Fairbridge and Ross[53] 's result that final weight loss of wood sawdust was independent of temperature at the range below 300 °C in air. With the assumed fixed final weight loss and first-order reaction mechanism, from equations (1) and (2), each weight loss value could be described as a linear line in the plot of ln(t) against reciprocal of absolute heating temperature T. Figure 4.6 showed the residue lines of Kapor and Nyatoh wood at 40% residual weight and 30% residual weight. At this stage, the wood turned into well-burnt char and might initiate self ignition [18]. The lines allowed predictions of heating durations needed to achieve this well-burnt char stage at lower temperatures or higher temperatures. For example, from the lines, it could be predicted that at 130 °C, Kapor wood took approximately 650 days to reach 40% residual weight and 1146 days to reach 30% residual weight while Nyatoh wood takes 2403 days and 3007 days respectively. At higher temperature, for example at 220 °C, these values were 14.5 days and 21 days for Kapor wood and 2 days and 5 days for Nyatoh wood correspondingly.



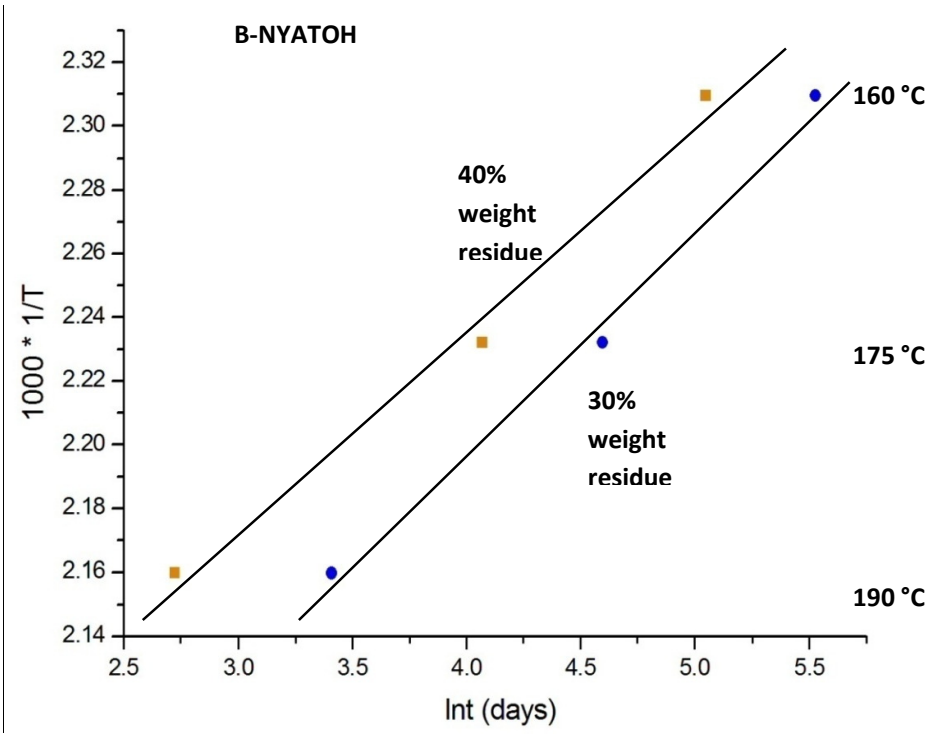


Figure 4.6. Plots of 1/T versus ln(t) of A-Kapor and B- Nyatoh wood.

4.5. Concluding remarks

The main findings of wood pyrolysis included:

- After exposure to low temperatures for long durations, visible physical changes happened to Kapor and Nyatoh wood blocks like cracks, colour darkening and shrinkage. The rate of weight loss was observed to be fast initially and slowed down with time.
- Wood blocks heated in vacuum conditions degraded less comparing with those heated in air conditions. This is due to the lack of oxidative activities in vacuum condition.
- Elemental analysis showed that dehydration contributed to the initial fast weight loss of the wood blocks. The loss of functional groups containing predominantly oxygen and oxygen was reflected through the increase of carbon content and decrease of oxygen and hydrogen contents.
- The rate of weight loss decreased with heating time until it reached the value of zero; this is the final weight when the wood chars became stable. Through graphic extrapolation, final weight of Kapor and Nyatoh wood heated in air at 160 °C, 175 °C and 190 °C were in the range of 19-25%.
- The kinetics of wood weight loss was shown to follow a first-order reaction. The kinetic model could be used to predict the heating time for wood to reach different stages of pyrolysis at certain low temperature and helped to prevent the potential of self ignition.

CHAPTER 5

Characterization of wood chars

5.1. Introduction

This chapter had two main parts. The first part discussed the functionality of the chars using FTIR experimental results. The second part described the chemisorptions characteristics of the chars. Both Kapor and Nyatoh wood chars were analyzed at different heating conditions: aerobic and anaerobic environments, heating time and heating duration. All the findings about char functionality and chemisorptions characteristics were summarized in the concluding remarks.

5.2. Infrared spectroscopic analysis

5.2.1. Kapor wood chars

Wood chars created in anaerobic condition

Figure 5.1 showed the FTIR spectra of wood chars heated in vacuum. The spectra of wood after thermal treatment in vacuum showed relatively good stability of the material at 175 °C up to 26 days. The most noticeable change of the heated samples comparing to the untreated samples was the decrease of intensity of absorption band near 1730 cm^{-1} attributed to carbonyl stretching of ester and carboxyl groups. Absorption of hydroxyl band at 3400 cm^{-1} also decreased. This was probably due to the decomposition of these oxygenated groups: decarboxylation, de-esterification and de-hydroxylation to release water and CO_2 to form ether. There was a slight

increase of ether band at 1220 cm^{-1}. Elemental analysis from Table 4.3 also showed that contents of hydrogen and oxygen decreased with time when heated in vacuum condition indicating the removal of water and CO_2.

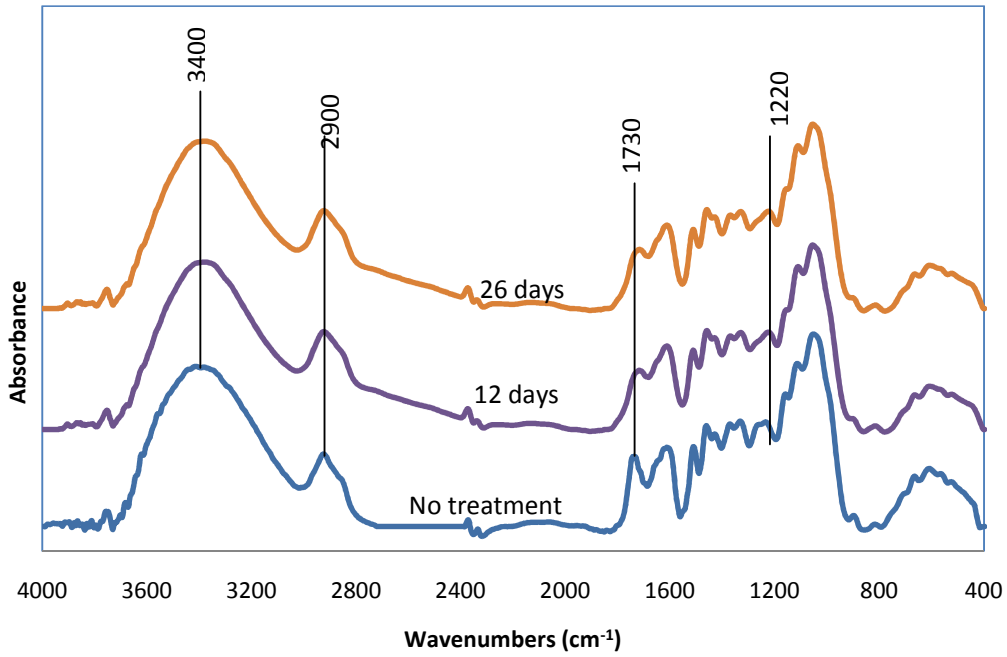


Figure 5.1. FTIR spectra of Kapor wood chars heated in vacuum at 175°C for different duration.

Wood chars created in aerobic condition

The trend of spectral changes taking place during the process of thermal degradation in air was similar at each heat treatment temperature (160 °C, 175 °C and 190°C); the degree of changes depended on temperature and duration of treatment. Figures 5.2 and 5.3 showed examples of similar spectra obtained from the wood chars heated at 160 °C and 175 °C for extended durations. Same initial spectrum of untreated sample could be spotted in both figures.

There was a broad band at 3400 cm^{-1} in every char spectrum. Since the samples were oven-dried for 24 hours, water content was minimized, the absorption band at 3400 cm^{-1} was mainly due to hydroxyl groups including phenol and alkyl OH. There was an initial increase in hydroxyl absorption at 3400 cm^{-1} followed by a gradual decrease as the duration was extended. The likely explanation for this phenomenon was the initial formation of hydroxyl groups by oxidation followed by condensation of these groups to form ether and ester linkage [62].

There was also a progressive decrease of absorption of aliphatic stretching at 2923 cm^{-1} and aliphatic bending at 1450 cm^{-1} with increasing temperature and duration. The intensities of these aliphatic bands were very weak after 12 days at 175 °C and 87 days at 160 °C and the bands were completely removed after 69 days at 175°C and 110 days at 160°C. In addition, the absorption at 1730 cm^{-1} arising from carbonyl and carboxyl groups' formation increased dramatically with heating duration. All of these changes could be explained by the oxidation of aliphatic groups to form oxygenated groups (hydroxyl, carbonyl, carboxyl, and ester) and it was also observed that at higher temperature, the rate of oxidative reaction was faster.

A remarkable increase in intensity of the band near 1600 cm^{-1} was observed after heat treatment in air indicating the increase of aromaticity of the chars. There was also a large shift from bands 900-1200 cm^{-1} to higher frequency band peak at 1260 cm^{-1} as reaction time progressed. This was due to the decomposition of glycosyl units and formation of ether structures. When the glycosyl bands totally disappeared, the chars became stable and only varied in intensity with longer heating time.

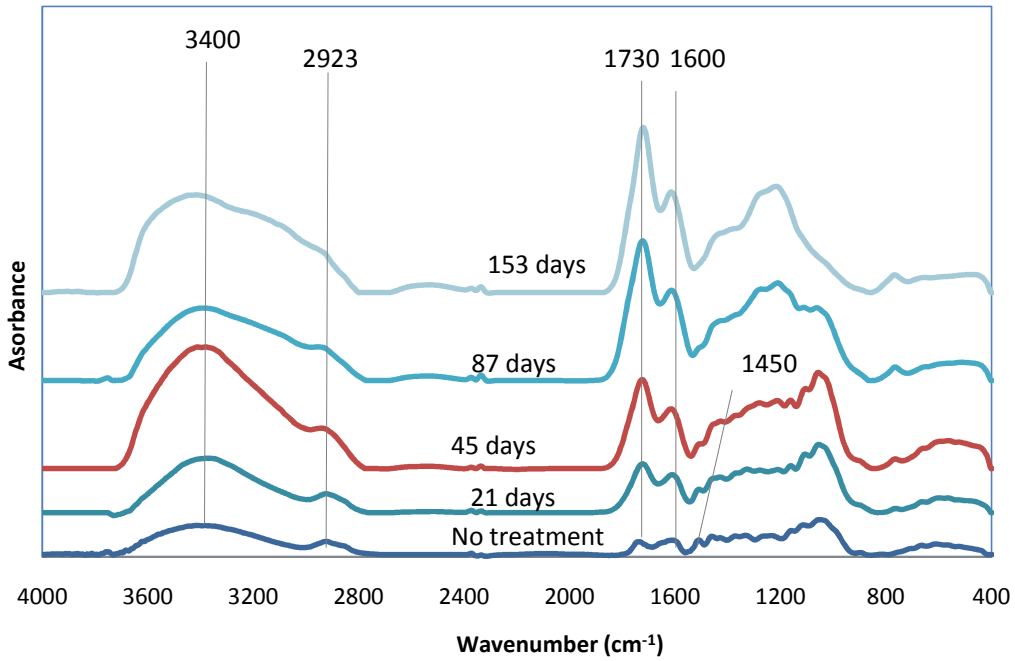


Figure 5.2. FTIR spectra of Kapor wood chars heated in air at 160°C for different duration.

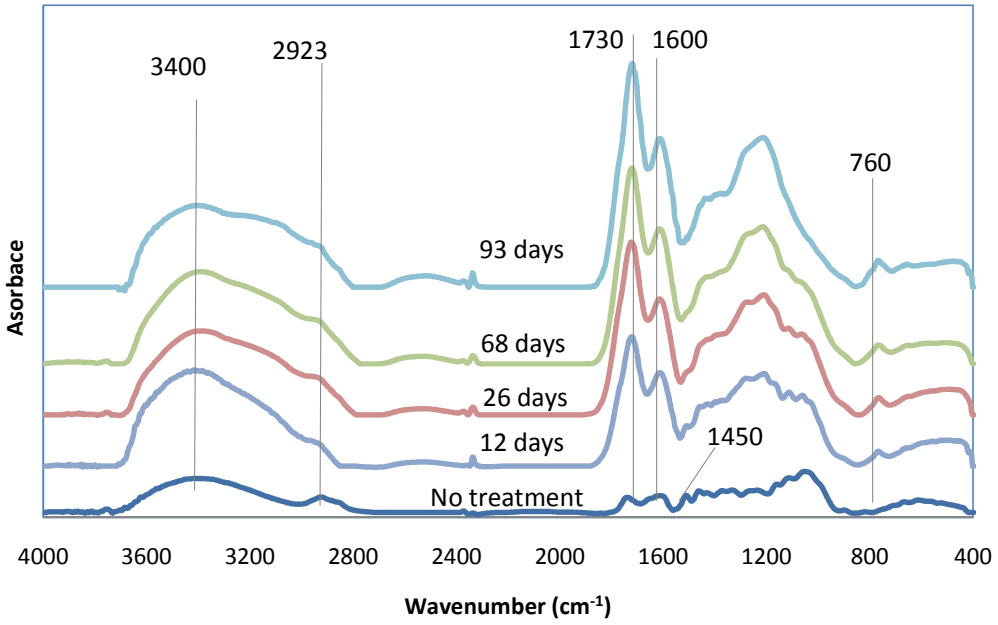


Figure 5.3. FTIR spectra of Kapor wood chars heated in air at 175°C for different duration.

For the aromatic C-H out-of-plane stretching zone between 700 and 900 cm^{-1}, the most striking change was the loss of 870 cm^{-1} band characteristic for isolated

aromatic ring hydrogen and 810 cm^{-1} band characteristic for two or three neighbouring aromatic ring hydrogen, and the appearance of a new band at 760 cm^{-1} signifying four neighbouring aromatic ring hydrogen. The intensity of the 760 cm^{-1} band increased linearly upon further heating. The degree of aromatic substitution could be revealed through the number of neighbouring hydrogen on an aromatic ring. More neighbouring aromatic ring hydrogen indicated that the degree of substitution was lower as reaction progressed. This was attributable to decarboxylation reactions as suggested by Calemma et al. [32]. The decarboxylation reactions removed carboxyl groups and replaced these with aromatic ring hydrogen; as a consequence less substituted aromatic structures were formed.

$$C_6H_n(COOH)_{6-n} \rightarrow C_6H_4(COOH)_2 + (4\text{-}n)\ CO_2$$

Comparison between anaerobic and aerobic chars

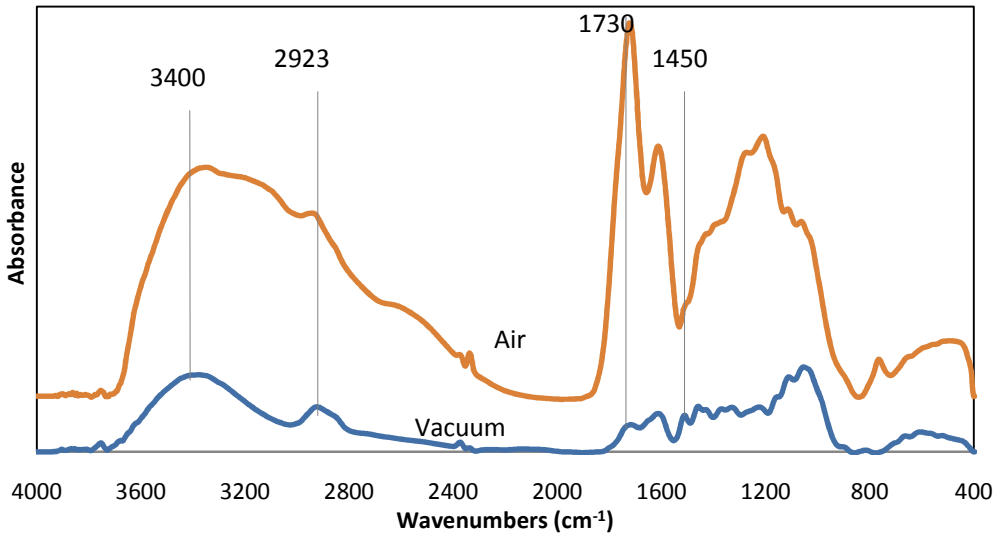


Figure 5.4. Comparison of FTIR spectra of Kapor wood char heated at 175°C for 12 days in air and vacuum condition.

From the current experimental data, the tendencies of structural changes in wood chars heated in air were quite different from those heated in vacuum with all other conditions being equal (Figure 5.4). When heated in air, beside thermal pyrolysis, the chars were also subjected to oxidation; thus, while the oxygen-containing groups kept decreasing in vacuum-heated wood chars, they were abundant in air-heated wood chars.

5.2.2 Nyatoh wood chars

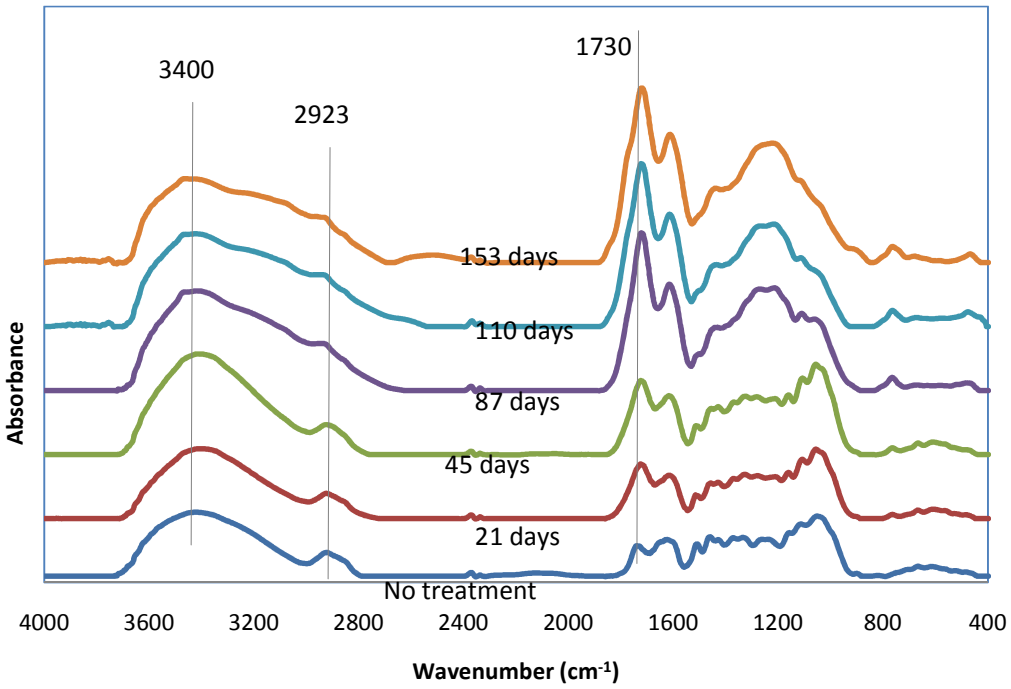


Figure 5.5. FTIR spectra of Nyatoh wood chars heated in air at 160°C for different duration.

Figure 5.5 showed an example of the change in spectra of Nyatoh wood char heated in air at 160 °C for different durations up to 153 days. Heat treatment in air at 160 °C, 175 °C and 190 °C of Nyatoh wood produced the same changes in functional groups as Kapor wood; however, the rate of variation of each group was

a bit different. For example, absorbance of 1730 cm^{-1} band increased initially and then decreased slightly after a long period (after 87 days), this was due to the effect of two concurrent factors happening during thermal degradation in air: oxidation and decomposition. For Nyatoh wood, initially, the rate of oxidation reaction was greater, thus, the absorbance of 1730 cm^{-1} band kept increasing; however, after a period of time, the rate of decomposition of the oxygenated groups (carbonyl and carboxyl) was greater, as a result, the absorbance of 1730 cm^{-1} band decreased slightly.

5.2.3. Comparison of wood chars before and after chemisorption

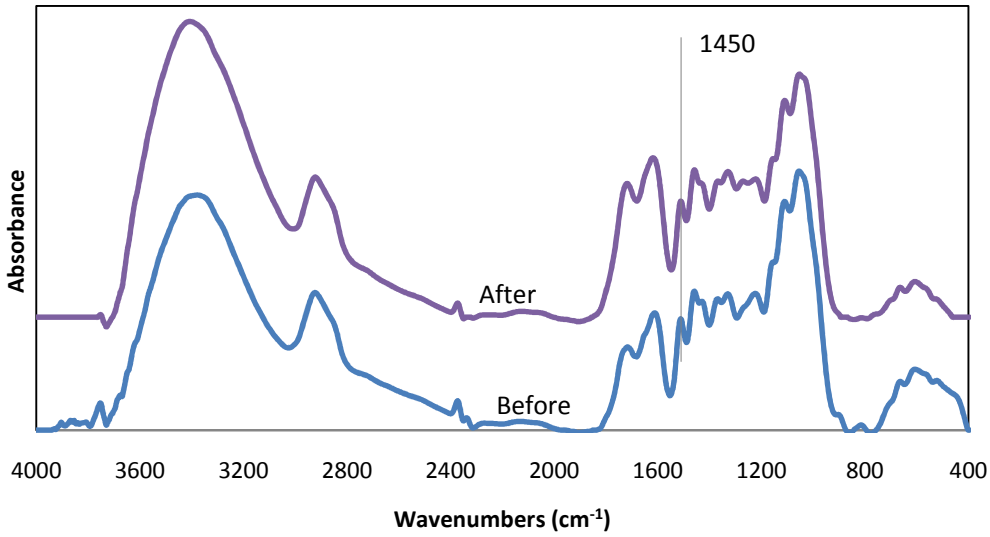


Figure 5.6. FTIR spectra of wood chars heated in vacuum at 175°C for 26 days before chemisorptions and after chemisorptions in air at 50°C for 10 hours.

After chemisorption in air at low temperatures in the range 40-60°C, the chars heated in air showed only little variations in FTIR spectra because oxidation had already happened during the treatment at 175°C. For chars heated in vacuum condition, the spectral modifications were more obvious after oxygen chemisorption. This supported TGA results in the next section that anaerobic chars

had more active sites available for chemisorptions. Figure 5.6 illustrated the changes occurring to wood chars heated in vacuum at 175°C for 26 days and then exposed to air at 50°C for 10 hours. As the reaction proceeded, spectra showed a general increase in adsorption due to oxygenated groups at 3400 cm^{-1} (hydroxyl) and 1730cm^{-1} (carboxyl). Concurrently, there was also a decrease in aliphatic stretching (2923 cm^{-1}) and bending (1450 cm^{-1}). More losses could be observed to aliphatic bending groups at 1450 cm^{-1} attributed to α-CH_2 bending to aromatic ring. This indicated that aliphatic groups, especially α-CH_2 to aromatic ring were highly reactive towards oxygen even at very low temperature. However, since the chemisorptions temperatures were at very low range 40-60°C, the reaction rate was very slow and there was still abundance of aliphatic groups. This provided an explanation for the small amount of oxygen uptake during chemisorptions in the next section on Chemisorption. In addition, the disappearance of the aromatic structures in the range 700 - 900 cm^{-1} after chemisorption suggested that benzylic and hydroaromatic groups were also very reactive to oxygen. This was in agreement with the findings of Hshieh and Richards [34] and Furimsky et al. [63].

5.3. Oxygen chemisorption of wood chars

At CST 70 °C, weight loss was observed after initial weight gain. This indicated desorption and gasification which happened concurrently with chemisorption. It was difficult to separate the amount of weight loss due to chemisorption or gasification; therefore, chemisorption kinetics could not be calculated for the 70°C data set. At CSTs 40 °C, 50 °C and 60 °C, in most cases, weight loss was not detected. A simple test was carried out to check desorption and gasification by replacing air with nitrogen at the end of each chemisorption run. The recorded

weight varied insignificantly, hence, the weight gain was assumed to be resulted from oxygen chemisorption.

Figures 5.7, 5.8 and 5.9 showed the oxygen adsorption data obtained at CSTs 40 °C, 50 °C and 60 °C of Kapor wood chars preheated in vacuum and air conditions. The chars were designated as K175-26V-40, K175-26V-50, K175-26V-60 (for char preheated at 175 °C for 26 days in vacuum) and K175-26A-40, K175-26A-50, K175-26A-60 (for char preheated at 175 °C for 26 days in air) and K175-93A-40, K175-93A-50, K175-93A-60 (for char preheated at 175 °C for 93 days in air) according to heat treatment condition and CST respectively. In all cases, the chemisorption rate was most rapid at the beginning right when the char was first exposed to air and decreased with time following Elovich kinetics. It was because oxygen adsorption only occurred at reactive groups and the chemisorption process gradually removed these reactive groups. The process started with the most reactive groups followed by groups with decreasing reactivity [63]. There would be no further oxygen adsorption at steady state when all the active sites became saturated. In this study, saturated state was not reached during experimental period (up to 12 hours). Besides, the study also showed that chemisorption reaction was an activated process [25], at higher temperature, the initial rate of adsorption was faster and the amount of oxygen chemisorption was greater.

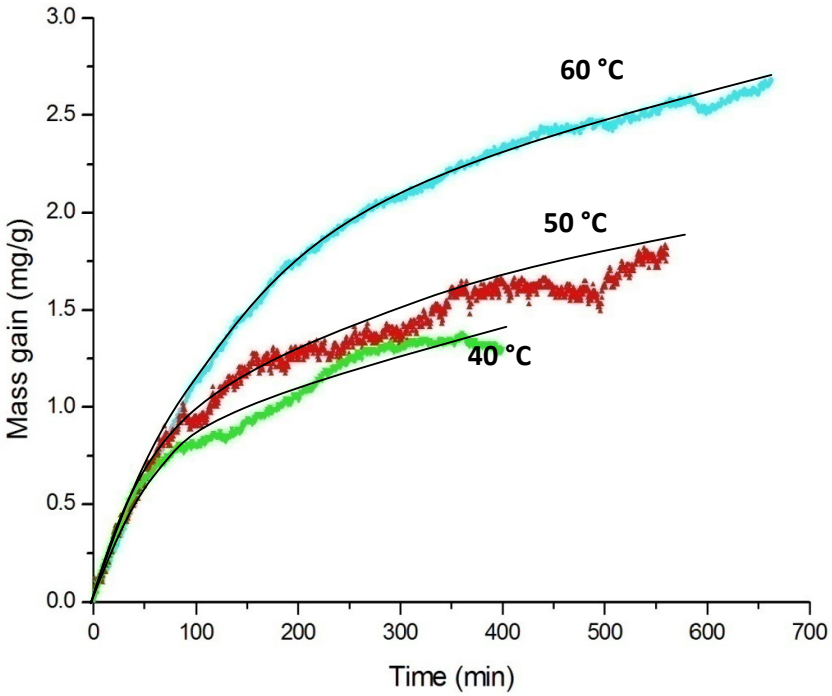


Figure 5.7. Mass gain during chemisorption of oxygen at different isothermal temperatures of Kapor wood char preheated at 175 °C for 26 days in vacuum.

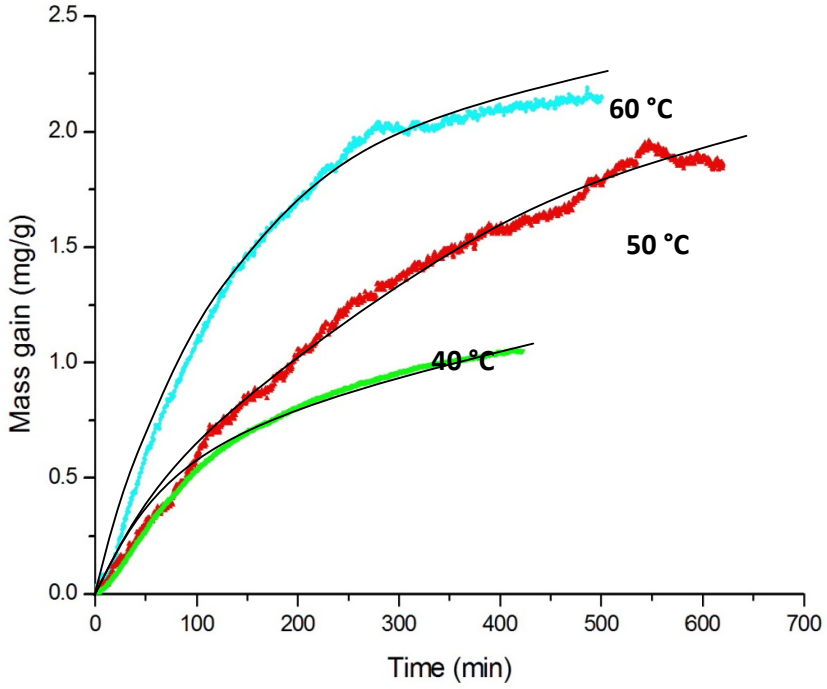


Figure 5.8. Mass gain during chemisorption of oxygen at different isothermal temperatures of Kapor chars preheated at 175 °C for 26 days in air.

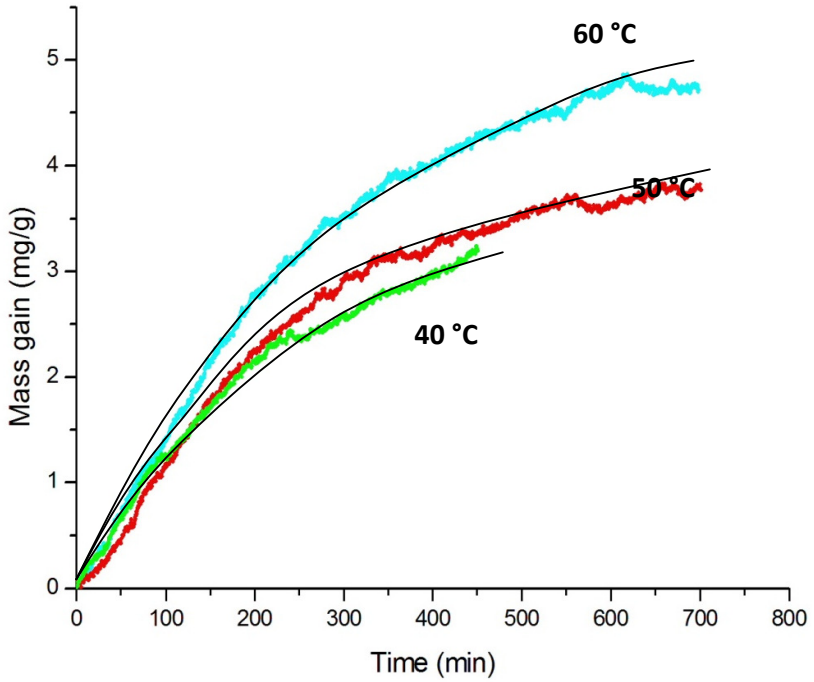


Figure 5.9. Mass gain during chemisorption of oxygen at different isothermal temperatures of Kapor chars preheated at 175 °C for 93 days in air.

Kinetics of chemisorption of oxygen on char surfaces has been analyzed by Elovich equation. This equation could be written as:

$$\frac{dw}{dt} = a\ exp(-bw) \qquad (5)$$

Where:

a = Elovich constant (mg/g min)

b = Elovich constant (g/ mg)

t = time (min)

w = weight due to amount of oxygen absorbed (mg/g)

According to McLintock [36], w=0 at t=0, equation (5) became:

$$w = \left(\frac{1}{b}\right) ln(1 + abt) \qquad (6)$$

or

$$w = \left(\frac{1}{b}\right) ln(t + t_0) - \left(\frac{1}{b}\right) ln(t_0) \qquad (7)$$

where t_0= *1/ab*.

Constant t_0 was the period of rapid chemisorption that preceded the Elovichian period, it linearized plots of w versus ln(t+t_0) [7, 41]. Iteration method was applied to find an empirical value of t_0 that gave the best fit to Elovich plot *w* against $ln(t + t_0)$ of the data given in Figures 5.7, 5.8 and 5.9. Values of *b* and *a* were calculated from the slope and intercept of the line obtained respectively. Table 4.5 summarized all the calculated values of Elovich contants of Kapor wood chars at different conditions. Figures 5.7, 5.8 and 5.9 also illustrated the solid lines which corresponded to the simulated data using the calculated Elovich parameters. These curves were observed to fit well with most of the experimental data, this confirmed that the chemisorption process of these chars followed Elovich kinetics and the adsorption sites were heterogeneous.

Table 5.1. Elovich constants for oxygen chemisorption on wood chars preheated at 175°C in air and in inert conditions.

Samples	CST (°C)	*a* (mg g^{-1} min^{-1})	*b* (mg^{-1} g)
K175-26V-40	40	0.024	2.240
K175-26V-50	50	0.027	1.979
K175-26V-60	60	0.032	1.217
K175-26A-40	40	0.009	1.546
K175-26A-50	50	0.010	1.216
K175-26A-60	60	0.020	1.019
K175-93A-40	40	0.018	0.512
K175-93A-50	50	0.024	0.631
K175-93A-60	60	0.024	0.399

The constant *a* was the initial rate of oxygen chemisorption at *w*=0. It could be observed from Table 5.1 that *a* was dependent on temperature, a higher initial chemisorption rate occurred at higher chemisorption temperature for both aerobic chars and anaerobic chars. This was due to the presence more reactive groups available for oxygen chemisorptions at higher temperature. At lower temperature, only the highly reactive groups were accessible. Table 5.1 also showed the amount of mass uptake after 400 minutes, for both aerobic and anaerobic chars, there was more mass gain at higher chemisorption temperature.

Comparing anaerobic chars and aerobic chars preheated for the same duration 26 days, at the same CST, anaerobic char had greater initial rate of oxygen chemisorption (Table 5.1). Even aerobic char preheated for 93 days also had lower initial rate of oxygen chemisorption than anaerobic chars preheated for 26 days. This indicated that anaerobic char possessed higher intrinsic reactivity towards oxygen than aerobic chars. This was in agreement with FTIR results, anaerobic char and aerobic char had different chemical structures. While in aerobic chars, the reactive groups like aliphatic α-CH_2 or aliphatic –CH_3 had already taken part in oxidation process when preheating in air, these reactive groups were still abundant in anaerobic chars and ready for oxygen chemisorption.

Comparing aerobic chars heated for different durations, at the same CST, char preheated for 93 days had higher initial rate of chemisorption than char preheated for 26 days (Table 5.1) indicating the increase of reactivity of the chars with increasing preheating time in air. From FTIR results, benzylic and hydroaromatic groups were the main reactive sites responsible for the oxygen chemisorptions of

aerobic chars. The increase in reactivity of 93-day char could be explained by the increase of aromatic structures of this char in comparison with 26-day char.

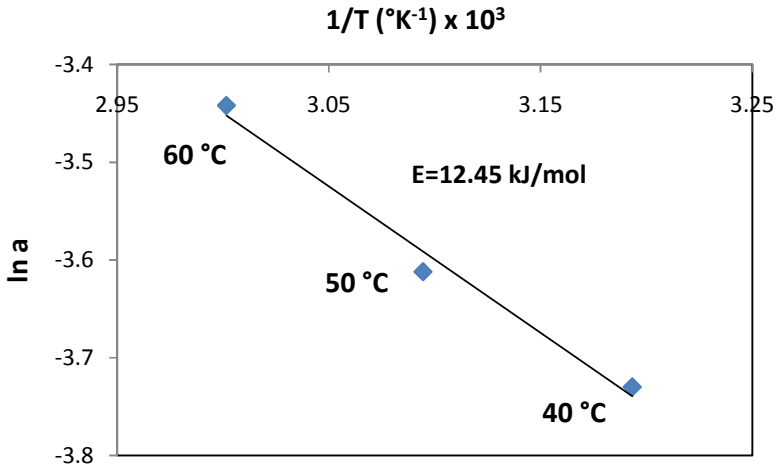


Figure 5.10. An Arrhenius plot of oxygen chemisorption of Kapor chars preheated at 175 °C for 26 days in vacuum.

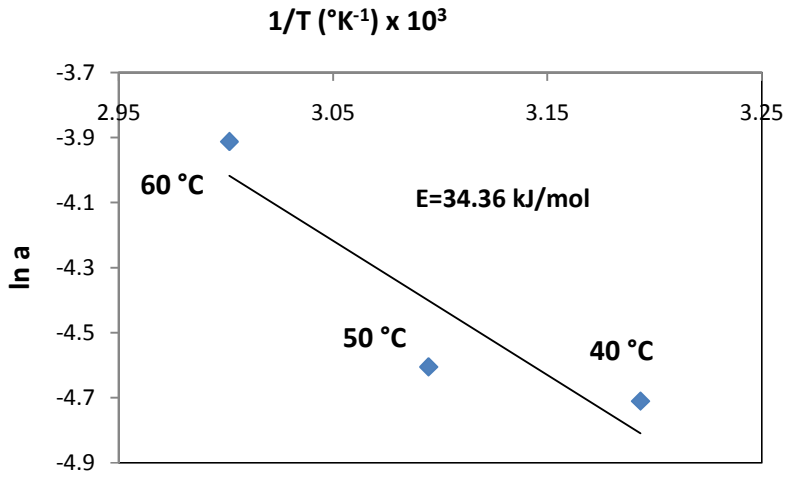


Figure 5.11. An Arrhenius plot of oxygen chemisorption of Kapor chars preheated at 175 °C for 26 days in air.

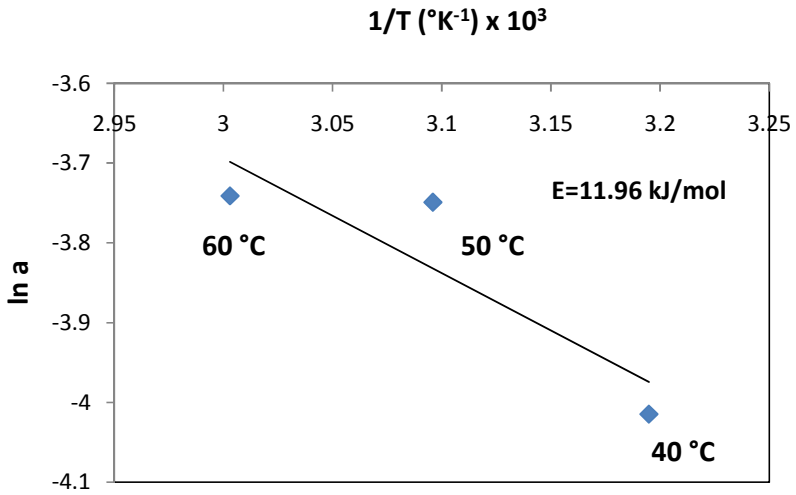


Figure 5.12. An Arrhenius plot of oxygen chemisorption of Kapor chars preheated at 175 °C for 93 days in air.

The rates and extents of oxygen chemisorption found in this study were lower comparing with other studies on cellulosic materials. From Table 5.2, it was found that the quantity of oxygen uptake and initial rate of oxygen chemisorption of the chars were one order of magnitude lower than those reported previously using cotton wood, cellulose and coal chars. The reason was partly due to the lower heat treatment temperatures and chemisorption temperatures. While most other studies used chars prepared at 375°C and above for very short duration, this study focused on chars preheated for very long duration at low temperature. Moreover, this study used air instead of oxygen; in this case, rates of chemisorption were reduced by a factor of 5 less than the amount absorbed under oxygen conditions [25].

Table 5.2. Comparison of quantity of oxygen chemisorption and initial chemisorption rate between present study and other studies in literature.

Char	HTT (°C)	CST (°C)	W (mg/g)	a (mg/g min)	Reference
Cottonwood chars	375	140[a]	12.8 (=0.4 mmol/g)	0.352 (=0.011mmol/g min)	(Hshieh and Richards 1989) [64]
Cellulose chars	550	74		0.1472 (=0.0046mmol/g min)	(Bradbury and Shafizadeh 1980) [31]
Coal chars	500	100[b]	30	0.5423	(Khan 1990) [65]
Anaerobic wood chars	175	60[c]	2.52	0.032	**Present study**
Aerobic wood chars (26 days)	175	60[c]	2.03	0.020	**Present study**

[a] Chars were exposed to oxygen for 2 hours.
[b] Chars were exposed to oxygen for 10 hours.
[c] Chars were exposed to air for 10 hours.

Using the values of *a* at different CSTs, the activation energies could be determined from Arrhenius plot of ln *a* versus 1/T as illustrated in Figures 5.10, 5.11 and 5.12. From the slopes, the values obtained for activation energies of initial oxygen chemisorption were 12.45 kJ/mol for anaerobic 26-day char, 34.36 kJ/mol for aerobic 26-day char and 11.96 kJ/mol for aerobic 93-day char. The magnitudes of activation energies of Kapor wood chars in both anaerobic and aerobic conditions were small; however, some others researchers also reported low range of activation energies. Suuberg et al. found the activation energies in the range 0-57 kJ/mol for resin char [66] and Khan et al. obtained activation energies in the range 4-63 kJ/mol for coal chars [65]. The low activation energies could be attributed by mass transport or diffusion rate control. However, the range of investigated temperatures 40- 60°C was too low for diffusion progress of oxygen molecule through a surface firm of nitrogen gas or through the pores to absorption sites. It was suggested that low activation energies could be resulted from the surface re-arrangement of

absorbed species with the migration of a mobile physically adsorbed layer across the surface to active sites where chemical interaction occurred and the conversion of physically absorbed oxygen to a chemisorbed oxygen [42].

5.4. Concluding remarks

The main findings on characterization of wood chars include:

- Oxygen-containing groups kept decreasing in vacuum-heated wood chars while they were abundant in air-heated wood chars. This was because the chars were subjected to both pyrolysis and oxidation when heated in air.
- After exposure to oxygen at low temperatures in the range 40-60 °C, the spectra of wood chars showed that adsorption due to oxygenated groups increased while those attributable to aliphatic α-CH_2, benzylic and hydroaromatic groups decreased. It is obvious that aliphatic α-CH_2, benzylic and hydroaromatic groups were reactive toward oxygen.
- The oxygen chemisorption process of wood chars was proved to follow Elovich kinetics. A higher chemisorption rate occurred at higher chemisorption temperature for both aerobic chars and anaerobic chars.
- It was also shown that the reactivity of wood chars depended on preheating conditions. Wood chars heating in anaerobic conditions had higher initial rate of chemisorption at the same CST, thus, they are more reactive than aerobic chars. For aerobic chars, the reactivity increased with the heating time, this could be explained by the increase in reactive aromatic structures with time.

CHAPTER 6

Conclusions and Recommendations

6.1. Conclusions

This thesis has been an attempt to address the pyrolysis and propensity to self ignition of long term low temperature wood chars. In doing so, pyrolysis experiments were carried out in ovens on two kinds of hardwood species Kapor and Nyatoh in both anaerobic and aerobic conditions. The heating temperatures were chosen at 160 °C, 175 °C and 190 °C and experimental periods were extended up to 153 days (5 months). The propensity to self ignition was investigated through oxygen chemisorption characteristics and functionality of aerobic and anaerobic wood chars. The results of wood pyrolysis and wood reactivity including functionality and oxygen chemisorption were shown to be consistent and support each other. The main findings can be listed as follows:

1. When wood specimens were heated at low temperatures for long durations, changes occurred to their both physical and chemical structures. The degree of changes was dependent on heating temperature and duration of heating treatment. The physical changes included the darkening of colour and development of transverse shrinkage and cracks. Chemical changes leaded to weight loss of wood specimens. The final

weight of the Kapor and Nyatoh wood heated in air at 160°C, 175°C and 190°C were calculated to be in the range 19-25%.

2. Pyrolysis kinetic models of Nyatoh and Kapor wood under isothermal conditions in air were developed based on the weight loss. Thermal degradation of wood samples in the study followed a first order reaction process after the initial period of fast degradation. The pyrolysis kinetic model was useful to predict the heating period to reach different degrees of degradation under air condition as the function of temperature of Nyatoh and Kapor wood. The activation energies of the two kinds of hardwood used in this study were different although these values were still in the range reported in literature. The activation energies of Kapor and Nyatoh wood found in this study were 77.5 kJ/mol (18.52 kcal/mol) and 102.8 kJ/mol (24.6 kcal/mol) respectively. The difference in activation energy was due to the different in rate of decomposition. Heating in exactly the same condition, this difference could be explained by the different chemical compositions of Kapor and Nyatoh hardwood with different proportion of cellulose, hemicelluloses and lignin. This reflected that chemical composition of wood played a critical role in the pyrolysis progress.

3. Chemisorption evidences revealed that chars created at low temperature for long duration (175°C for 26 days and 93 days) in both aerobic and anaerobic conditions chemisorbed oxygen at low CSTs 40 °C, 50 °C and 60 °C. Thus, these chars were reactive and prone to self ignition.

4. From FTIR results, it was proposed that aliphatic α-CH_2, benzylic and hydroaromatic groups were especially reactive with oxygen and played as the first abstraction sites for oxygen chemisorption at very low temperatures.

5. Anaerobic wood char (preheated for 26 days) was found to possess higher intrinsic reactivity towards oxygen in comparison with aerobic wood chars (preheated for 26 days and 93 days) signifying by higher initial rate of oxygen chemisorption at the same chemisorption temperature. This could be explained by the availability of more reactive aliphatic groups, especially aliphatic α-CH_2, ready for oxygen chemisorption in anaerobic char. For less reactive aerobic char, because the reactive aliphatic groups were totally removed from the chars after 93 days, it was possible that benzylic and hydroaromatic groups were the reactive sites responsible for the oxygen chemisorption.

6. It was reflected in chemisorption results that the higher the degree of pyrolysis, the more reactive the char became. 93-day wood char (weight loss 64.3 %) was shown to have higher initial rate of oxygen chemisorption in comparison to 26-day wood char (weight loss 34.8 %). It was obvious that when wood was exposed to low temperatures for long durations, the changes in chemical structure affected its reactivity and self heating characteristics, the higher the degree of pyrolysis, the more reactive the char became. This was supported by FTIR results of the possible increase of reactive benzylic and hydroaromatic groups in aerobic chars with pyrolysis time in air. With this, the chars would

become most reactive when it reached the charcoal condition at the final weight around 19-25%. The rates and extents of oxygen chemisorption found in this study were one order of magnitude lower comparing to cellulosic and coal chars reported in previous studies. This was due to the much lower heat treatment temperatures and chemisorption temperature. In addition, the use of air instead of oxygen during chemisorption experiments reduced the rate of chemisorption by a factor of 5. Activation energies of oxygen chemisorption were calculated using Arrhenius equation and yielded results in the range of published results. However, these values were rather small and in the lower-end range. It was suggested that low activation energies could be resulted from the surface re-arrangement of absorbed species with the migration of a mobile physically adsorbed layer across the surface to active sites where chemical interaction occurred and the conversion of physically absorbed oxygen to chemisorbed oxygen.

In conclusion, the thesis provided the experimental evidences for the pyrolysis and reactivity of wood chars created at low temperatures for long durations and evaluated their hazards to ignition. Thermal degradation of wood samples in the study followed a first order reaction process after the initial period of fast degradation and it was proved that the chars would become most reactive when they reached the charcoal condition at the final weight around 19-25%. Both aerobic and anaerobic wood chars were shown to be reactive toward oxygen. The level of reactivity depends on preheating conditions. Chars being heated in anaerobic conditions and for longer

time were found to be more reactive. Chemical groups responsible for the oxygen chemisorption included aliphatic α-CH_2, benzylic and hydroaromatic groups.

The theoretical understanding had practical meaning to the use of wood in related to fire safety and fire protection. In addition, with the widespread application of Nyatoh and Kapor wood, especially in tropical countries, the pyrolysis kinetic model of these woods was significant to predict the heating period as a function of temperature in air before reaching the final charcoal stage where self ignition was most probable to take place and the risk of fire was high.

6.2. Recommendations for future works

Although results of this study provided significant understanding on the pyrolysis and reactivity of long term low temperature wood chars, there remained areas where research needed to be performed.

It was suggested that different kinds of wood had different rate of pyrolysis, thus, the kinetic data vary with the species of wood. The study investigated the pyrolysis kinetic data of Kapor and Nyatoh wood and helped to predict the heating period to reach different degrees of degradation under air condition as the function of temperature of these two kinds of wood. However, there was still a lack of kinetic data of other wood species. It is recommended to apply the model and method used in this study to obtain the kinetic data of other wood species based on weight loss history.

Most self ignition cases to wood members happened when the wood was closed to low heat sources like hot water pipes, hot operating machines and hot air ducts. The effect of the heat sources to wood members might be constant or periodic. The study provided experimental data for the reactivity of long-term low-temperature wood chars heated isothermally in oven. Additional experimental data on the reactivity of wood chars created in periodic heating conditions would give a complete investigation on reactivity and self ignition propensity of the wood chars.

An insight to the oxygen chemisorption results of wood char was examined using FTIR analytical method. Further effort is needed to inspect the reaction sequences and mechanisms during chemisorption process. This can be done by a constant

measurement of the functionality and the evaporated gases of the char throughout the whole process of oxygen chemisorption.

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APPENDICES

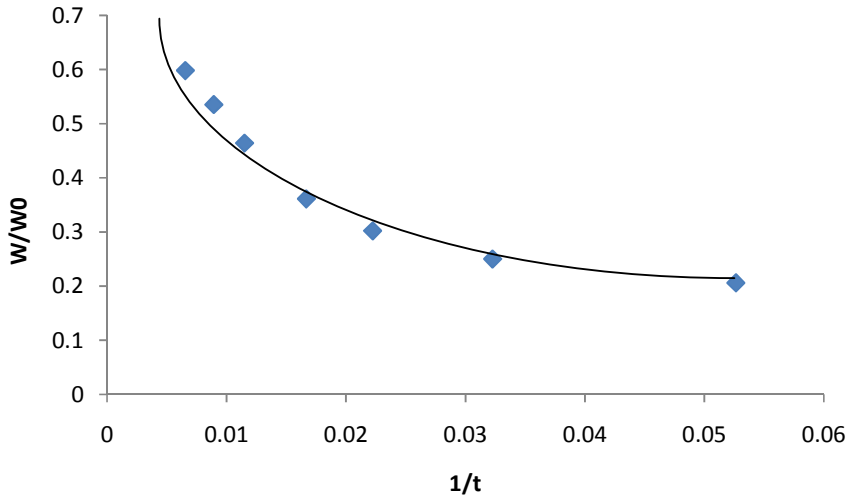
APPENDIX 1

Final weight determination of pyrolyzed Kapor and Nyatoh Wood chars:
Using iteration method.

1. Kapor wood :

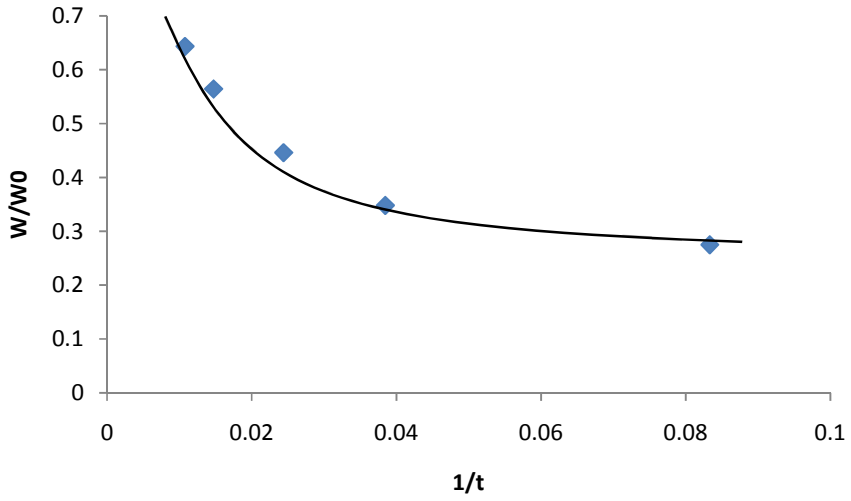
At 160 °C: $\frac{W_\infty}{W_0}$**= 21.58%**

t (day)	1/t	$\frac{W_0 - W}{W_0}$
19	0.052632	0.206
31	0.032258	0.25
45	0.022222	0.302
60	0.016667	0.361
87	0.011494	0.464
112	0.008929	0.535
153	0.006536	0.598



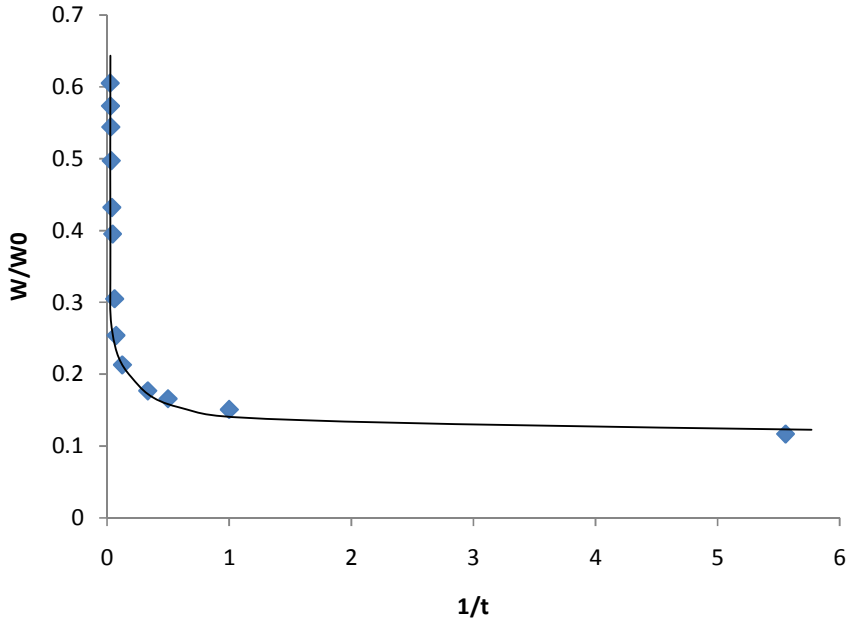
At 175 °C: $\frac{W_\infty}{W_0}$**= 21.47%**

t (day)	1/t	$\frac{W_0 - W}{W_0}$
12	0.083333	0.275
26	0.038462	0.348
41	0.02439	0.446
68	0.014706	0.564
93	0.010753	0.643



At 190 °C: $\frac{W_\infty}{W_0}$= 18.68%

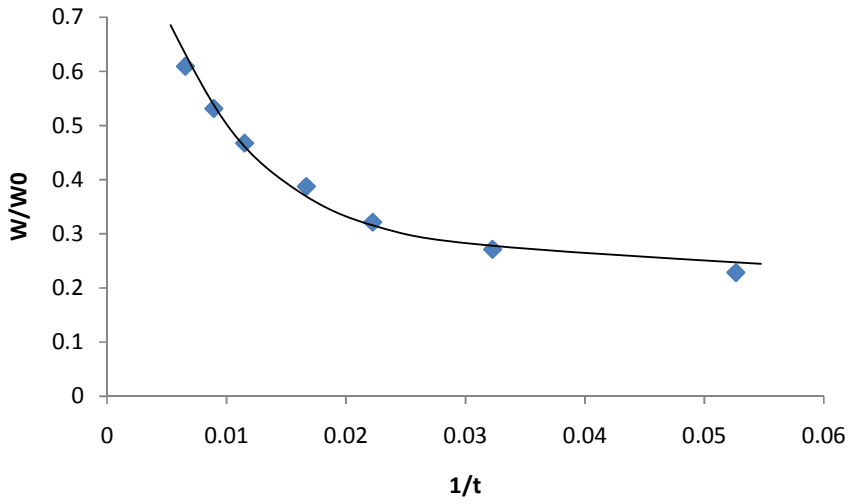
t (day)	1/t	$\frac{W_0 - W}{W_0}$
0.18	5.555556	0.117
1	1	0.151
2	0.5	0.166
3	0.333333	0.177
8	0.125	0.213
13.5	0.074074	0.254
16	0.0625	0.305
22	0.045455	0.395
25	0.04	0.432
29	0.034483	0.497
33	0.030303	0.544
36	0.027778	0.573
40	0.025	0.605



2. <u>Nyatoh wood :</u>

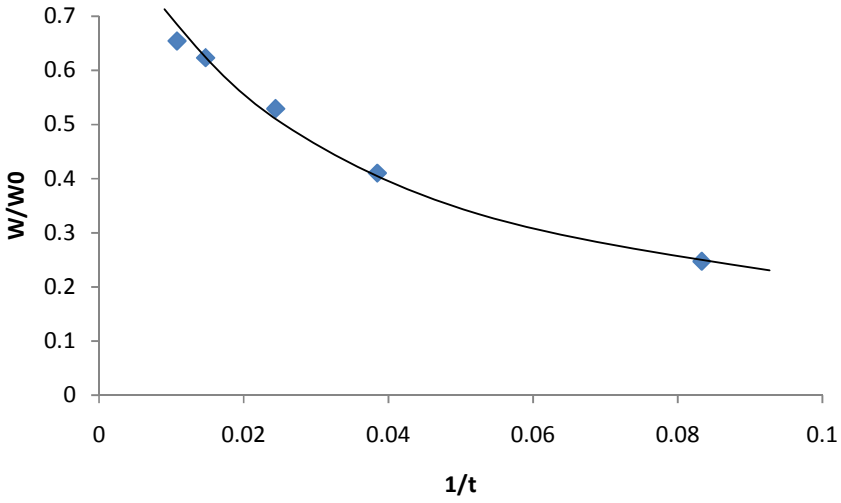
At 160 °C: $\frac{W_\infty}{W_0}$= 20.74%

t (day)	1/t	$\frac{W_0 - W}{W_0}$
19	0.052632	0.228
31	0.032258	0.271
45	0.022222	0.321
60	0.016667	0.387
87	0.011494	0.467
112	0.008929	0.531
153	0.006536	0.609



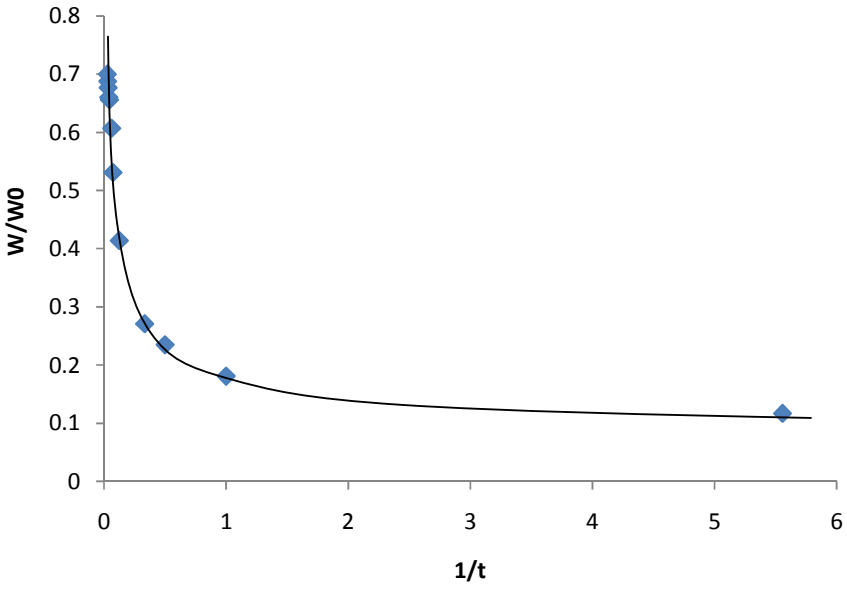
At 175 °C: $\frac{W_\infty}{W_0}$= 24.4%

t (day)	1/t	$\frac{W_0 - W}{W_0}$
12	0.083333	0.247
26	0.038462	0.41
41	0.02439	0.529
68	0.014706	0.623
93	0.010753	0.654



At 190 °C: $\frac{W_\infty}{W_0}$= 23.67%

t (day)	1/t	$\frac{W_0 - W}{W_0}$
0.18	5.555556	0.117
1	1	0.181
2	0.5	0.235
3	0.333333	0.271
8	0.125	0.414
13.5	0.074074	0.531
16	0.0625	0.607
22	0.045455	0.656
25	0.04	0.66
29	0.034483	0.677
33	0.030303	0.688
36	0.027778	0.7



APPENDIX 2

Calculation of the value of the kinetic constant k for the pyrolysis of wood based on weight loss:

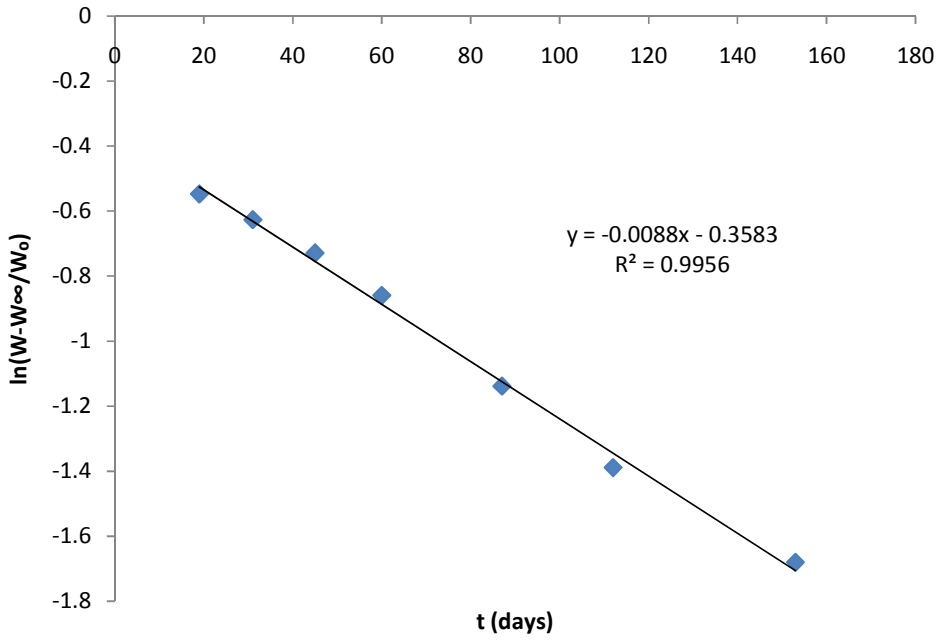
The value of k could be obtained by plotting $\ln\left(\frac{W-W_\infty}{W_0}\right)$ against t according to the equation:

$$\ln\left(\frac{W-W_\infty}{W_0}\right) = \ln\left(\frac{W_i-W_\infty}{W_0}\right) + kt_i - kt$$

1. Kapor wood:

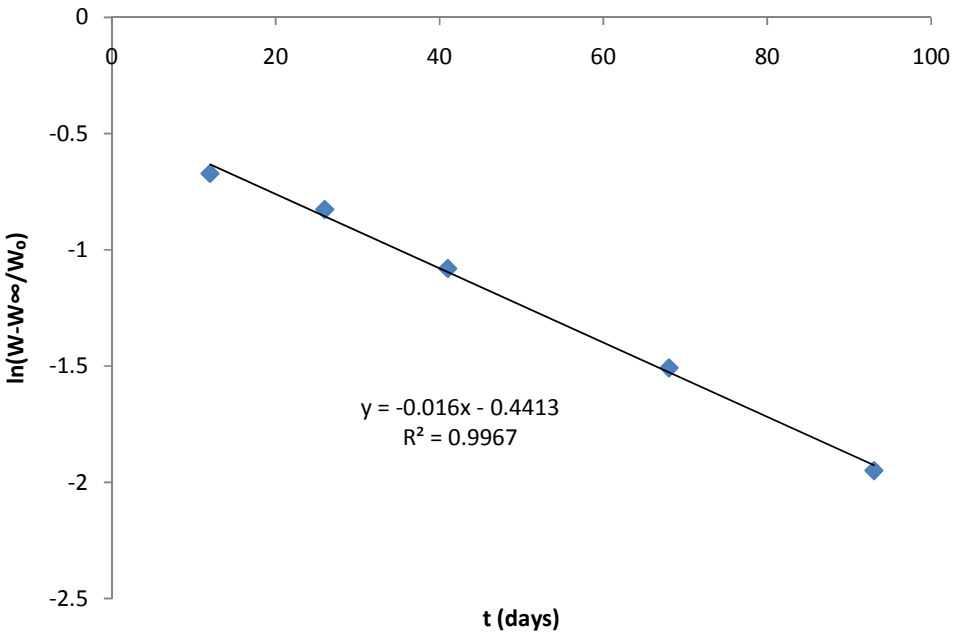
At 160 °C: k = 0.0088

t (day)	$\frac{W}{W_0}$	$\frac{W-W_\infty}{W_0}$	$\ln\left(\frac{W-W_\infty}{W_0}\right)$
19	0.794	0.5782	-0.54784
31	0.75	0.5342	-0.62698
45	0.698	0.4822	-0.7294
60	0.639	0.4232	-0.85991
87	0.536	0.3202	-1.13881
112	0.465	0.2492	-1.3895
153	0.402	0.1862	-1.68093



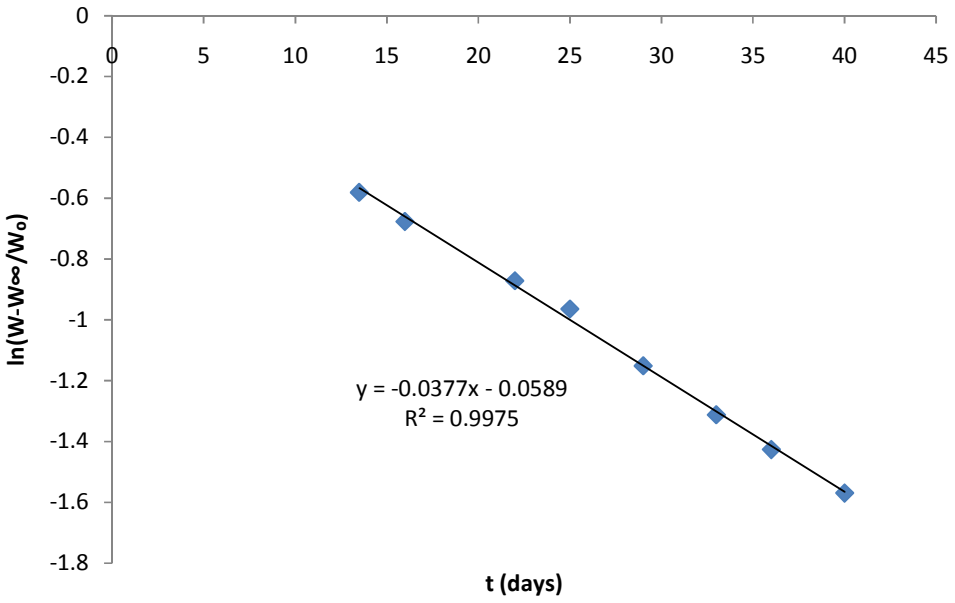
At 175 °C: k = 0.016

t (day)	$\frac{W}{W_0}$	$\frac{W - W_\infty}{W_0}$	$\ln\left(\frac{W - W_\infty}{W_0}\right)$
12	0.725	0.5103	-0.67276
26	0.652	0.4373	-0.82714
41	0.554	0.3393	-1.08087
68	0.436	0.2213	-1.50824
93	0.357	0.1423	-1.94982



At 190 °C: k = 0.0356

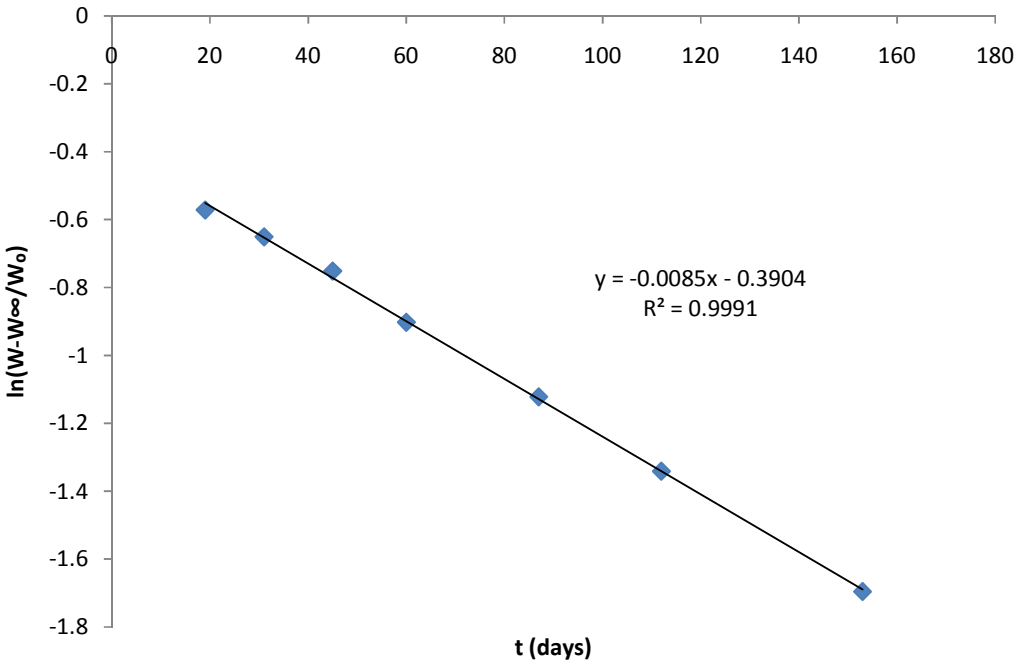
t (day)	$\frac{W}{W_0}$	$\frac{W - W_\infty}{W_0}$	$\ln\left(\frac{W - W_\infty}{W_0}\right)$
13.5	0.746	0.5592	-0.58125
16	0.695	0.5082	-0.67688
22	0.605	0.4182	-0.8718
25	0.568	0.3812	-0.96443
29	0.503	0.3162	-1.15138
33	0.456	0.2692	-1.3123
36	0.427	0.2402	-1.42628
40	0.395	0.2082	-1.56926



2. Nyatoh wood:

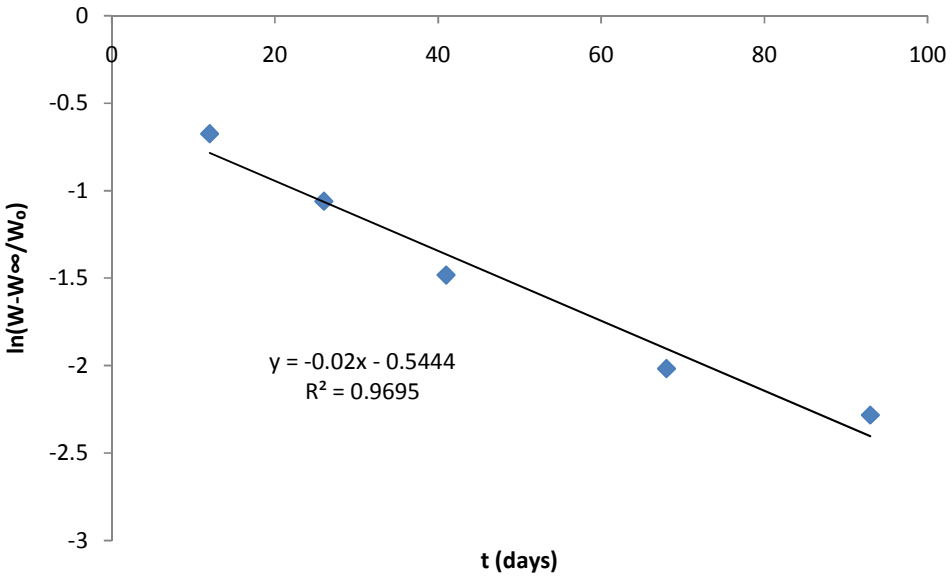
At 160 °C: k = 0.0085

t (day)	$\frac{W}{W_0}$	$\frac{W - W_\infty}{W_0}$	$\ln\left(\frac{W - W_\infty}{W_0}\right)$
19	0.772	0.5646	-0.571637763
31	0.729	0.5216	-0.650854268
45	0.679	0.4716	-0.75162411
60	0.613	0.4056	-0.902387827
87	0.533	0.3256	-1.122085645
112	0.469	0.2616	-1.340938659
153	0.391	0.1836	-1.694995801



At 175 °C: k = 0.02

t (day)	$\frac{W}{W_0}$	$\frac{W - W_\infty}{W_0}$	$\ln\left(\frac{W - W_\infty}{W_0}\right)$
12	0.753	0.509	-0.675307262
26	0.59	0.346	-1.061316504
41	0.471	0.227	-1.482805262
68	0.377	0.133	-2.017406151
93	0.346	0.102	-2.282782466



At 190 °C: k = 0.0542

t (day)	$\frac{W}{W_0}$	$\frac{W - W_\infty}{W_0}$	$\ln\left(\frac{W - W_\infty}{W_0}\right)$
13.5	0.469	0.2323	-1.459725639
16	0.393	0.1563	-1.855978042
22	0.344	0.1073	-2.232126629
25	0.34	0.1033	-2.270117903
29	0.333	0.0963	-2.34028696
33	0.312	0.0753	-2.586275144
36	0.3	0.0633	-2.75986995